Solid Phase Microextraction Field Deployment and Analysis Work Plan

Pacific Sound Resources Superfund Site
Seattle, WA

Prepared For:

Region 10
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1.0 Problem Statement and Purpose

Dissolved-phase groundwater contamination and "fingers" of NAPL were known at the time of the Pacific Sound Resources (PSR) Superfund Site 1998 RI/FS to extend from the Upland Unit containment wall area towards the Marine Sediments Unit in Puget Sound. The ROD determined that, based on modeling, dissolved-phase contaminants associated with these NAPL fingers were not likely to impact sediment or surface water protectiveness. However, EPA has noted both new NAPL detections and exceedances of ROD-specified contaminant thresholds in groundwater shoreline wells, which indicates potential risk of contaminated groundwater discharge through the placed sediment cap to surface water. A determination of whether dissolved-phase contaminants impact surface water quality at PSR is necessary to confirm both current and future remedy protectiveness. In short, it is currently unknown (a) whether dissolved-phase contaminants currently or will likely in the future impact surface water quality at PSR and (b) if potentially mobile NAPL detected beyond and below the slurry wall could reach the mudline. Results of the following three activities will be used to develop a multiple lines of evidence approach required to assess sediment and surface water contamination from site groundwater; however, this PWS only applies to the first activity.

(1) Collect and analyze porewater samples in areas of most-likely contaminated groundwater discharge to surface water and compare results to surface water criteria. Due to site constraints (variable cap depths and water depths), a passive porewater sampler program is recommended for this purpose.

(2) Collect and analyze surface sediment grab samples collocated with porewater samples to evaluate sediment quality, determine compliance with sediment standards, and assess equilibrium partitioning between porewater and sediment-associated phases. If the theoretical porewater/sediment equilibrium is greatly exceeded, this could indicate advective discharge of contaminated groundwater.

(3) Collect seepage velocity measurements in areas corresponding to the proposed porewater/sediment sampling to quantify rate of groundwater discharge to surface water.

The purpose of the work described in this work plan is to collect/analyze porewater samples in areas of most-likely contaminated groundwater discharge to site sediment and surface water. The U.S. Environmental Protection Agency (USEPA) Region 10 has requested the Seattle District, U.S. Army Corps of Engineers (USACE) to plan for and deploy the vertical-profiling solid-phase microextraction (SPME) technology in order to determine the extent of creosote-related porewater contamination in the sediment and capped sediments at the site. This PWS describes SPME field deployment, analysis and results reporting required to quantify PAHs in PSR site sediment porewater. Results will be used to determine if contaminated site groundwater is currently impacting sediment porewater and surface water quality in areas of most likely groundwater-to-surface water discharge pathways.

2.0 Porewater Sampling at PSR using SPMEs

2.1 Technology Description

SPMEs consist of a sorbent polymer layer (polydimethylsiloxane or PDMS) of approximately 10 to 30 μm in thickness surrounding a glass core with thickness of 100-1000 μm (the smallest fibers are similar to the thickness of a human hair). The SPMEs are typically deployed directly into sediment inside perforated stainless steel PushPoint sampling devices (Figure 1). Rapid uptake of PAHs and PCP in the fiber occurs without interference of colloidally-bound contaminants, and this provides an improved measure of dissolved COC concentrations in porewater. Porewater provides a direct measure of bioavailable contaminants in sediment, and indicates potential exposure for benthos and pelagic organisms and thus relevant ARARs compliance.

Deployed SMPEs would be allowed to equilibrate with sediment porewater for a minimum of 7 days before retrieval, which is a suitable period of equilibration time as determined by experience with comparable projects. Upon retrieval, the SPME fibers are cut into sections, extracted, and analyzed. The resulting SPME concentrations are converted to corresponding porewater concentrations using the regression relationships developed and reported in the SPME Calibration Study Report (Appendix A). Porewater concentrations are then compared to surface water ARARs for PAHs as shown in Table 4. Porewater concentrations will also be used to estimate corresponding sediment concentrations using equilibrium partitioning equations.

2.2 Data Quality Objectives

Data gaps, project objectives and investigation methods are summarized in Table 1below. Referenced concentration ranges and analytical sensitivities for SPME porewater analysis are summarized in Table 4. As described in the table below, co-located sediment grab samples will be collected during the SPME deployment and will be submitted to a separate laboratory for analysis of PAHs. While data quality objectives for the sediment samples are described here, detailed laboratory analysis requirements for PAHs will be conducted by a separate laboratory and will be described in an addendum to this work plan. Additional sediment sample volume will also be archived should analysis of other sediment COCs (PCBs, PCP, metals) be desired as well. Methods for sediment grab sample collection, handling and archiving are provided in Section 2.3.

Table 1. Data Quality Objectives

Data Gap	Project Objectives	Investigation Methods	Performance Goal	Decision Criteria
Is Elliott Bay sediment porewater currently contaminated with PAHs due to contaminated groundwater discharge from PSR Superfund Site?	Measure sediment porewater concentrations of PAHs directly downgradient of shallow groundwater discharge from areas where > 1 ft of NAPL staining was observed beyond the slurry wall during the RI/FS (RETEC 1998).	Insert SPME fibers up to 3 ft below the sediment surface and allow for equilibration with sediment porewater for 7 days. Retrieve SPMEs and section into discreet sample depth intervals (in the 0-4, 4-8, and 20-24 inches below sediment surface intervals), preserve sections immediately in acetonitrile, and submit for analysis of PAHs.	Detection limits for PAHs at or below surface water quality standards or as otherwise indicated in Table 4.	Compare measured PAHs concentrations in the 0-4 and 4-8 inch SPME sections to surface water quality standards to assess compliance with ARARs and current impacts to near-surface sediment porewater. Results of deeper porewater sections may indicate future cap contamination. If deeper contamination is detected, seepage velocity values may be used to calculate contaminant flux and time to potential contaminant breakthrough.
Do surface sediment concentrations of PAHs, in the vicinity of the proposed porewater sampling locations meet SQS criteria? Sediment monitoring was not conducted in the proposed areas during the 2007 Long-Term Monitoring Event due to a presumption that the placed sediment in these areas was clean.	Measure surface sediment concentrations of PAHs in the subject areas to determine compliance with SQS criteria.	Collect co-located surface sediment grab samples in 8 oz. glass jars and submit for analysis of sediment PAHs and total organic carbon. Total organic carbon is a required input parameter for calculating porewater/sediment equilibrium partitioning values. All sediment samples will be archived pending SPME porewater results, which will be used as a basis to select subset of sediment samples to submit for analysis of PAHs.	Detection limits for PAHs at or below SQS standards or as otherwise indicated in Table 4.	Compare measured concentrations of PAHs in sediment to SQS criteria to determine whether current conditions meet cleanup requirements. Sediment concentrations will also be used to determine whether chemical equilibrium exists between sediment and porewater concentrations.

2.3 Field Deployment Methods

2.3.1 SAMPLING LOCATIONS

SPMEs will be deployed in twenty four locations as indicated on Figure 2. The western array is located downgradient from upland groundwater monitoring wells MW-5 and MW-14 series, which contain NAPL or elevated concentrations of PAHs (RETEC 2005). Samples in the eastern array are located down gradient of known NAPL impacted areas beyond the slurry wall containment area and downgradient from monitoring well MW-15IR, which was observed to contain NAPL during a September 2008 sampling round (USACE 2009). In addition, two SPMEs will be deployed to measure surface concentrations in the water column. Surface water SPMEs will be attached to the top of a stainless steel push-point sampler, which will be inserted into the sediment so that the SPME fiber is suspended approximately 1 ft above the sediment surface in the water column. Surface water SPMEs will be located between SPME locations PSR 10 and PSR 4 in the western array and between PSR 17 and PSR 22 in the eastern array (Figure 2) and will remain deployed for the duration of the field test to ascertain if there are systemic exceedances for PAHs in surface water. An additional regional background and upgradient SPME surface water sample location was selected in West Seattle where there are no known nearby sources of PAHs. The background surface water sample will also be suspended approximately 1 ft off the sediment bottom and will be located ~ 100 ft from the pilings of the nearby condominium building (Figure 3). The background surface water sample will be linked with cord to a select piling beneath the condo so that the divers may follow the cord to easily relocate the background sample during retrival.

Surface sediment samples will be collected at each SPME sampling location following SPME insertion at a radial distance of 1 ft from the SPME insertion location. A 1 ft clearance is provided so that the sediment surface grab sampling does not impact SPMEs following insertion.

2.3.2 INSERTION TOOL PREPARATION

Before deployment, all SPME sampling devices (i.e. the insertion tool) will be cleaned with Alconox detergent and distilled water, then subsequently rinsed with hexane, acetonitrile and distilled water. The insertion tool should then be subjected to a final distilled water rinse. Once cleaned the components of the insertion tool are packaged together, inner and outer sheath and placed aside for installation of SPME fiber.

SPME fiber should be cleaned before being inserted into the insertion tool with high purity solvents that will be used to extract contaminants for post-retrieval chemical analysis (i.e. acetonitrile). Cleaning the fiber consists of sonicating pre-cut lengths of fiber in acetonitriletwice each for 10-15 minutes. The acetonitrile is disposed of and the fibers are rinsed with distilled water and a clean wipe. The rinse with distilled water will help to remove any acetonitrile residuals left on the fiber but any remaining residuals will quickly evaporate from the

fiber. The stainless steel tubing in which exposed samples will be returned to the laboratory should be cleaned in a similar manner.

The cleaned fiber is laid into a groove cut into the inner rod of the insertion tool using tweezers (see Figure 4). Silicon serves to hold the fiber in place and can also be used to fill any gaps at the ends of the insertion tool to eliminate any water movement vertically. Care should be taken to avoid any placement of silicon on the screened length or active measurement portion of the insertion tool or to place so much silicon that cured silicon will hinder insertion tool separation after field exposure. To make sure the fiber is securely in place, a finger should be run along the groove. In addition, the grooved rod can be held vertically to check for any SPME fiber movement. If the fiber moves during either test, the process of installing the fiber should be repeated.

Once it is clear the fiber is securely in place, the inner and outer rods of the insertion tool should be placed side by side to determine the point on the outer rod which marks the top of the fiber and mark this with a wrapping of waterproof electrical tape. The inner rod with the fiber is then inserted into the outer sheath with groove and fiber aligned with the screened side of the sheath. The handles on both inner grooved rod and sheath are then wrapped together so the two sets of handles will not twist relative to each other causing the SPME fiber to become misaligned with the screened section of the outer sheath. The length of fiber that was loaded into each of the insertion tools should be documented.

2.3.3 NUMBERING

When inner rod and sheath are assembled, forming the complete SPME loaded insertion tool, handles are wrapped with electrical tape and a numbering system is constructed to keep a record of which rod was placed in what location. Different color tape can help aid with identifying planned location of deployment. Each completed insertion tool is numbered on the taped portion of the handles and planned deployment location documented. Full insertion rod sample numbering will be as follows; see Table 2 for example sample designators.

ss-dddd-ll-xxy

- sss – site (Pacific Sound Resources, PSR)
- dddd – date (e.g. 061208 for June 12, 2008 deployment date
- ll- location (e.g. CS for control sediment, SW for surface water)
- xx- sample number (e.g. 1, 2…)
- y – duplicate designator (a or b)

Table 2. Example sample designators.

Sample Designator	Matrix	Description	Analyses
PSR-092210-1-1a	SPME	Primary sample, location 1, within 0-4” depth (3-5 cm designated as sample a, 5-7 cm field duplicate designated as sample b)	PAHs
PSR-092210-1-2a	SPME	Primary sample, location 1, within 4-8” depth (13-15 cm designated as sample a, 15-17 cm field duplicate designated as sample b)	“
PSR-092210-1-3a	SPME	Primary sample, location 1, within 20-24” depth (54-56 cm designated as sample a, 56-58 cm field duplicate designated as sample b)	“

PSR-092210-1-4a	SPME	Archive sample, within 32-36" interval or otherwise the 4" interval from the greatest depth below the 24" sample where possible. (84-86 cm designated as sample a, 86-88 cm field duplicate designated as sample b)	"
PSR-092210-BKGDSW-1	SPME	Sample deployed in the water column ~ 10 ft above the sediment surface near Alki Beach in area free of known creosote sources and upgradient of PSR site based on surface water circulation patterns in Elliott Bay.	"
SW-1	SPME	Sample deployed in the water column ~ 10 ft above the sediment surface in the western cluster of SPME locations at PSR.	"
SW-2	SPME	Sample deployed in the water column ~ 10 ft above the sediment surface in the eastern cluster of SPME locations at PSR.	"
PSR-092210-1	Sediment	Co-located surface sediment grab samples will be collected following SPME insertion at each location. The sediment grab will be collected from a distance of ~ 1ft from the SPME insertion location so as not to disturb the inserted SPME.	Archive at -20°C

2.3.4 DEPLOYMENT

Once received at the desired location, all SPME insertion tools are deployed. The insertion tools are inserted to the point marked on the outer sheath where the top of the fiber is within the device. Insertion tools are inserted perpendicular into the sediment so a profile can be achieved. If the objective is evaluating the variability in porewater concentrations across a site, the number of samplers required must meet different objectives. Although a porewater sampler necessarily averages over some volume depending upon the rate of porewater mixing at a site, the volume is still very small compared to the size of a site.

At the PSR site, the deployment will involve placement of up to 27, 42" insertion tools with a 36" sampling section. The 36" working length will be used to sample the regions 0-10 cm (0-4"), 10-20 cm (4-8"), and 51-61 cm (20-24") below the sediment surface. Samplers will be deployed by divers provided by the project sponsor. All insertion tools will be connected via nylon cording. The location of the cording will be marked at the surface with submerged crab pot buoys.

Sediment samples will be collected following SPME insertion at each sampling location. The samples will be collected by EPA divers in two 8 oz. glass jars at a distance of ~ 1 ft from the inserted SPME so as to not disturb the SPME following successful insertion. The divers will collect the sediment samples from the surface using a clean stainless steel spoon at each location. Surface sediment sampling depth will not exceed 4 inches below the sediment surface. The 8 oz. glass jars will be filled with DI water so as to be neutrally buoyant during the dive and the lids will not be closed tightly to allow for easy opening by divers at depth. Lids for all jars will be pre-labeled (2 jars per sampling location). The EPA divers will then provide the filled sediment jars to the sample processing crew for labeling and storage at 4°C pending delivery to the laboratory at the end of each field day for storage at -20°C. The sample preparation crew will pour off excess liquid and provide some headspace in the jars to allow for sample expansion when frozen. The sediment samples will be handled under standard chain of custody procedures.

2.3.5 RETRIEVAL

During retrieval, the SPME fibers are withdrawn from the sediment and brought to the surface and immediately transported by boat to the beach for processing. Field notes will be collected to document all variances from expected or design conditions as well as to confirm locations of the field deployable SPME insertion tools and sample ID. The insertion tools are dismantled and the fibers are extracted from the inner rod. Any observations should be noted including color changes that may be due to changes in sediment biogeochemistry or evidence of relative rotation of the inner support rod or sheath should be documented. Samples should be handled with care when extracting the fiber from the inner rod since the sediment particles will most likely be packed into the inner rod and the fiber may be difficult to extract. After removing the tape from the handles, the inner rod should be carefully and slowly removed and placed on a flat surface with the grooved side facing upwards. The SPME fiber should be located and carefully removed and placed on a clean, high contrast surface with position of the sediment-water interface noted. If the fiber is broken during removal care should be taken to maintain relative position of the pieces. Any missing pieces or length, if any, should be documented and the overall length of fiber recovered documented. The fiber should be gently wiped with a clean tissue and distilled water to remove any sediment particles. The fiber will be sectioned in the field into intervals corresponding to 0-4, 4-8 and 20-24 inches below the sediment surface (0-10, 10-20 and 51-61 cm, respectively) and 2 cm segments will be collected from within each of these SPME intervals. That is, from each 4 inch segment, the top 3-5 cm and 5-7 cm sections will be collected and immediately placed in separate vials containing 200 µL of acetonitrile to preserve and extract the samples. The 3-5 cm section within each depth interval will serve as the primary sample and the 3-5 cm section will serve as the field duplicate sample. This sectioning plan will result in a total of 3 primary samples and 3 field duplicate samples being collected at each SPME insertion location. In addition, where SPME insertion depth allows, the 32-36 inch fiber depth interval will be collected and the top 3-5 and 5-7 cm sections in that interval will be archived for analysis pending results of other fiber depth intervals. All other fiber sections that are not collected for analysis will be collected and returned to the UT laboratory where they will be used for other purposes. A detailed description of sectioning and on-site handling procedures are discussed below. Sectioned samples will be shipped to the University of Texas for analysis. Field blanks will be processed identically as the samples as described above.

2.4 Field Sample Processing Methods Following Retrieval

2.4.1 SPME PROCESSING AND ANALYSIS

For fiber cutting and analysis the following tools will be needed: small tweezers, single edged razor blade or capillary column cutter, , 100 µL micro pipette, ruler with cm increments, Kim-wipes, distilled water, 2 mL autosampling vials with glass inserts prefilled with 200 µL of

acetonitrile, sampling vial caps, and rack to hold sampling vials. All tools should be cleaned and solvent rinsed before using.

Vials should be labeled prior to fiber cutting with any preferred method as per the method described above at a minimum including location, sample number and duplicate indicator. The fiber should be cut into sections depending on the detection abilities of the instruments being used for analysis and the concentrations expected. For the 30 μm PDMS fibers with 1 mm glass core to be used in this study, a 2 cm length of fiber is expected for each analysis. Cutting should begin at the top and continue to the bottom.

The cut fibers should be placed in the autosampling vial with insert and a syringe needle used to push the fiber to the bottom of the vial if the small fiber is used such that when solvent is added, the entire fiber will be immersed. 210 μL of solvent (Acetonitrile for PAHs) will be prefilled into the sample vial to preserve and extract contaminants from the fiber. Testing has shown that extraction is essentially complete with gentle shaking of the vial after solvent addition for 30 seconds.

Solvent blanks (sample containers with acetonitrile but no SPME fiber) will be included to verify that there are no contamination issues prior to use. In addition, five calibration standards will be shipped with the sampling vials, treated the same way as the field samples, and analyzed to indicate the solvent loss or possible contamination during shipping and handling. Internal standards maybe added to each sample vial depending on the feasibility. The current internal standard used by the UT laboratory, decafluorobiphenyl, coelutes with pyrene. New internal standards were ordered and will be tested when available. However, the known concentrations of the calibration standards, internal standards are not imperative.

The sample can then be shipped to the University of Texas and analyzed. During analysis the vial is placed in an autosampler. PAHs at the University of Texas will be analyzed with a high performance liquid chromatography (Waters 2690 HPLC) with UV-Diode array detector and fluorescence detector will be used to measure the concentration of the extract. (EPA method 8310; SW-846 3rd edition, 1986). All 16 PAH priority pollutants, dibenzofuran, and 2-methylnaphalene will be analyzed using HPLC (acenapthylene is not detectable by fluorescent detection and higher detection limits than other compounds may be noted using UV detection (see calibration study, Reible 2010). In addition Benzo(g,h,i) perylene and Indeno(1,2,3-cd) pyrene are expected to coelute.

2.4.2 CUSTODY AND SHIPMENT

For shipping, the SPME rods Insertion tools should be loaded with SPME and constructed and shipped immediately before deployment to avoid potential sorption due to exposure to environmental contaminants. One SPME insertion tool should be prepared and shipped to the site but held back from deployment to serve as a field blank to identify possible contamination during shipping for placement. An additional blank will be deployed upon retrieval.

Processed SPME samples will be shipped to the laboratory (Table 3) in plastic coolers with packing materials. The SPMEs will be shipped under chain of custody procedures without refrigeration as samples will be preserved in acetonitrile immediately following collection.

Table 3. Laboratory shipping and contact information.

Laboratory	Shipping Address	Contact Information
Department of Civil, Architectural and Environmental Engineering University of Texas	University of Texas Austin, TX 78712	**Danny Reible**, Principal Investigator reible@mail.utexas.edu (512) 471-4642 **XiaoXia Lu**, Technical Lead XiaoXia Lu: lux@mail.utexas.edu (512) 471-5870

2.4.3 DISPOSAL OF INVESTIGATIVE DERIVED WASTES

Personal protective equipment (PPE) for the sampling (consisting of Nitrile gloves) and other disposables used during sample preparation will be packaged in plastic garbage bags and disposed in a solid waste bin. All samples and chemical preservatives will be disposed of as per University of Texas hazardous material handling requirements.

3.0 Analytical Methods and Quality Assurance Requirements

The analytical procedures to be used for fixed laboratory analyses are described in this section. The analytical methods and associated quality assurance/quality control (QA/QC) procedures were selected based on consideration of the project objectives. The analytical methods, calibration procedures, and QC measurements and criteria are based on current analytical protocols in the following:

- EPA SW-846 *Test Methods for Evaluation of Solid Waste,* in particular Method 3510 or 3520 (extraction) and 8310 (High Performance Liquid Chromatography)
- Department of Defense Quality Services Manual
- Laboratory-specific standard operating procedures (SOP)

The methods selected will be sufficient to meet the project objectives. Laboratory QA will be implemented and maintained as described in this plan and according to the laboratories' QA plans and SOPs. While a best effort will be made to achieve the project performance goals, there may be cases in which it is not possible to meet the specified goals. Any limitation in data quality due to analytical problems (e.g., elevated detection limits) will be identified to the attention of the USACE Technical Team Lead. In addition, this information will be discussed in the data evaluation report.

3.1 Laboratory Analytical Methods, Method Detection, Quantitation and Reporting Limits

The analytical methods to be used by the laboratories are described in this section. The analytical methods and associated quality assurance/quality control procedures were selected based on consideration of the project objectives. Note that co-located sediment samples collected by EPA divers will be archived for analysis of PAHs and other sediment COCs (PCBs, dibenzofuran and metals) in the future. Analytical requirements for the archived sediment samples will be addressed under a separate document.

SPMEs: Method: High-Performance Liquid Chromatography (HPLC) with a Fluorescence Detector FD. All samples will be analyzed by by ultraviolet and fluorescent detectors although depending upon sample concentration only one will generally be used to quantify samplers (fluorescent for low concentration range samples, UV for high concentration range samples) Appendix B includes a table of method detection and practical quantitation limits for SPME analysis of PAHs, dibenzofuran, and 2-methylnaphalene.

Sensitivity requirements for all methods and matrices are driven by the intended comparisons to ambient water quality criteria (at the low end) and to elevated concentrations expected to be present if a strong PAH source is nearby (at the high end). The field and laboratory methods

selected provide data of sufficient sensitivity to allow the project team to evaluate site conditions and meet the project objectives. Specific sensitivity requirements by target analyte in water are presented in Table 4. See Appendix B for an explanation as to how these analytical sensitivity requirements were established. The laboratory will report results for PAHs down to the Method Detection Limit.

The resulting SPME contaminant concentration will be converted to freely dissolved porewater concentrations using the regression equations established as part of the SPME Calibration Study Report (Appendix A).

3.1.1 METHOD DETECTION LIMIT

The MDL is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the compound or element concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the compound or element (Appendix B of 40 CFR 136).

3.1.2 METHOD QUANTITATION LIMIT

The MQL represents the value for which the laboratory has demonstrated the ability to reliably quantitate target compounds and elements within prescribed performance criteria for the method performed. Operationally, the MQL is equivalent to the concentration of the lowest calibration standard in the initial calibration curve.

3.1.3 METHOD REPORTING LIMIT

The MRL is a threshold value below which the laboratory reports a result of non-detected. It may be based on project-specific concentrations of concern, regulatory action levels, or sensitivity capability of method and instrument. The MRLs are adjusted based on the sample matrix and any necessary sample dilutions. Operationally, it is equivalent to the MQL adjusted based on the sample matrix and any necessary dilutions. Because of the general lack of matrix interferences by the SPME method, the MRL is expected to equal the MQL.

Table 4. Analytical performance standards for SPME samples

Parameter – Method	**Surface Water Quality Standards, µg/L**	**Low-Level Limits, µg/L**		**QC Acceptance Criteria**	
		MDL	**PQL**	**LCS CL %**	**LCS/LCSD RPD**
PAHs (SW-8310)					
Low Molecular Weight PAHs					

2-Methylnaphthalene	n/a	0.212	1.54	45-105	<25
Acenaphthene	$6.40x10^{2}$	0.335	0.732	35-105	<25
Anthracene	$2.64x10^{4}$	0.0515	0.322	40-110	<25
Fluorene	$3.46\ x10^{3}$	0.454	0.778	35-105	<25
Naphthalene	9.58	0.291	2.80	35-105	<25
High Molecular Weight PAHs					
Benzo(a)anthracene[c]	$1.80x10^{-2}$	$2.20x10^{-4}$	$5.70\ x10^{-4}$	50-110	<25
Benzo(a)pyrene[c]	$1.80x10^{-2}$	$1.10\ x10^{-4}$	$4.10\ x10^{-4}$	45-115	<25
Benzo(g,h,i)perylene[a, c]	n/a	$9.00\ x10^{-5}$	$2.70\ x10^{-4}$	35-120	<25
Benzo(b)fluoranthene[c]	$1.80x10^{-2}$	$3.90\ x10^{-4}$	$7.40\ x10^{-4}$	40-125	<25
Benzo(k)fluoranthene[c]	$1.80x10^{-2}$	$4.00\ x10^{-5}$	$4.60\ x10^{-4}$	45-125	<25
Chrysene	$1.80x10^{-2}$	$6.40\ x10^{-4}$	$1.29\ x10^{-3}$	50-115	<25
Dibenz(a,h)anthracene	$1.80x10^{-2}$	$3.00\ x10^{-5}$	$1.50\ x10^{-4}$	20-110	<25
Fluoranthene	90	$9.27\ x10^{-3}$	$6.13\ x10^{-2}$	50-115	<25
Indeno(1,2,3-cd)pyrene[a]	$1.80x10^{-2}$	$9.00\ x10^{-5}$	$2.70\ x10^{-4}$	45-110	<25
Phenanthrene	n/a	$4.93\ x10^{-2}$	$1.50x10^{-1}$	40-120	<25
Pyrene	$2.59x10^{3}$	$1.01x10^{-2}$	$3.38x10^{-2}$	50-110	<25
PAH Secondary Calibration Standard					
(Run At Initial Calibration; Relative to Primary Standard)					<15 [b]
Other Semivolatile Organic Compounds					
Dibenzofuran		$5.67x10^{-2}$	$5.79x10^{-1}$	65-135	<25

LCS – Lab calibration standard

LCSD – LCS duplicate

CL – Control limit

RPD – Relative Percent Difference

[a] – Benzo(g,h,i) perylene and Indeno(1,2,3-cd) pyrene co-elute and may not be analytically separated by the Laboratory, although efforts are underway to separate them.

[b] – This value is from the DOD QSM Table F2, for HPLC and water matrix.

c– The listed PQL is above the Surface Water Quality Standard concentration for these PAHs.

3.2 Quality Control

The overall quality assurance objective for field sampling and laboratory analysis is to produce data of known and appropriate quality to support the project objectives. Appropriate procedures and quality control checks will be used so that known and acceptable levels of accuracy and precision are maintained for each data set. Quality control samples are controlled samples introduced into the analysis stream whose results are used to review data quality and to calculate

the accuracy and precision of the chemical analysis program. The purpose of each type of quality control sample, collection and analysis frequency, and evaluation criteria are described in this section. Laboratory quality control samples as described in the referenced methods will be followed.

All quality control measurements and data assessment for this project will be conducted on samples from and within batches of samples from this project alone; in other words, no "other project" samples will be used with samples from this project for assessment of data quality.

3.2.1 FIELD QUALITY CONTROL SAMPLES

Field quality control checks are accomplished through the analysis of controlled samples that are introduced to the laboratory from the field and include trip blanks, field duplicates and matrix spike/matrix spike duplicate (MS/MSD) samples. In this study, **trip blanks** and **field duplicates** (based upon adjacent segments of the SPME fiber) will be analyzed. As described in Section 2.3.5, **field duplicates** will be collected for all samples from adjacent fiber depth intervals. However, experience has suggested that results for the field duplicate samples will correlate highly with results for primary samples. Their primary purpose is to identify sample problems (such as cap unsealed) that might lead to evaporation of the contents or other problems that will compromise individual samples. **Solvent blanks** will be analyzed at the time of filling of the vials for shipment, i.e. one at the start of filling and one at the end where the same solvent source has been used. If these contain PAHs at significant levels, new vials will be filled with a separate source and the process will be repeated. **Sampler and fiber contamination check samples** will also be tested at the start and end of the cleaning procedures and analyzed prior to shipment. In addition, there will be solvent blanks shipped with the samples at a frequency of 1 per 20 samples. **Field blanks** will be the samplers shipped with the other samples but not placed at the site. One field blank will be included per shipping container. A total of 5, 2 cm sections will be collected from each field blank sample. The 2 cm sections will be collected at even distances spaced along the fiber. Due to the nature of the SPME sampling, no matrix spikes will be employed.

3.2.2 LABORATORY QUALITY CONTROL SAMPLES

Laboratory QC checks are accomplished through analyzing initial and continuing calibration samples, method blanks, surrogate spikes, laboratory control samples (LCS), and laboratory duplicate samples.

Initial and Continuing Calibration Samples. Calibration of laboratory owned and operated equipment will be in accordance with the laboratory quality assurance/quality control plan as described herein and laboratory standard operating procedures (SOPs); see Appendix A for the following SOPs: total and dissolved organic carbon analysis, PAHs analysis by High Performance Liquid Chromatography, and liquid-liquid extraction for aqueous organics via separatory funnel.

Method Blanks. Method blanks are used to check for laboratory contamination and instrument bias. Laboratory method blanks will be analyzed at a minimum frequency of 5 percent or one per analytical batch for all chemical parameter groups. Quality control criteria require that no contaminants be detected in the blank(s) at concentrations greater than one-half the method quantitation limit (MQL) for target compounds and greater than the MQL for the common laboratory contaminants. If a chemical is detected, the action taken will follow the laboratory SOPs (provided in Appendix A). Blank samples will be analyzed for the same parameters as the associated field samples.

Surrogate Spikes. Not applicable.

Laboratory Control Samples. Not applicable. Calibration check standards will be used to compare to and these will be in the same solvent at similar concentrations as the analyzed samples and will be handled in field the same way that primary samples are handled. Our previous study (SPME Calibration Study) showed that extraction is almost complete (>99%) in a couple of minutes, so no LCS samples are needed. Calibration check standards are sufficient for evaluating potential loss and contamination during sampling.

Laboratory Duplicate Samples. Precision of the analytical system is evaluated by using laboratory duplicate samples. Laboratory duplicate samples are two portions of a single homogeneous sample analyzed for the same parameter. Laboratory duplicate samples will be prepared and analyzed with project samples as listed in laboratory SOPs.

Table 5. Quality Guidelines for Organic Analysis by High-Performance Liquid Chromatography (EPA 8310) from DOD QSM Version 4.1.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analyst capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method	QC acceptance criteria published by DoD, if available; otherwise method-specific criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria	NA	This is a demonstration of analytical ability to generate acceptable precision and bias per the procedure in Appendix A. No analysis shall be allowed by analyst until successful demonstration of capability is complete
MDL study	At initial set-up and subsequently once per 12-month period; otherwise quarterly MDL verification checks shall be performed	See 40 CFR 136B. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or re-conduct MDL study	NA	Samples cannot be analyzed without a valid MDL.
Minimum five-point initial calibration for all analytes (ICAL)	Initial calibration prior to sample analysis	One of the options below: Option 1: RSD for each analyte ≤ 20%; Option 2: linear least squares regression: r ≥ 0.995; Option 3: non-linear regression: coefficient of determination (COD) r2 ≥ 0.99 (6 points shall be used for second order, 7 points shall be used for third order).	Correct problem then repeat initial calibration.	NA	Problem must be corrected. No samples may be run until ICAL has passed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Continuing calibration verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analysis sequence.	All project analytes within established retention time windows. All project analytes within ± 15% of expected value from the ICAL	Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. Retention time windows are updated per the method.
Second source calibration verification (ICV)	Once after each initial calibration	All project analytes within established retention time windows. Value of second source for all analytes within ± 15% of expected value (ICAL)	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL	NA	Problem must be corrected. No samples may be run until calibration has been verified.
Evaluation of relative retention times (RRT)	With each sample	RRT of each target analyte in each calibration standard within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA	

Internal standards verification	In all field samples and standards	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL EICP area within - 50% to + 100% of ICAL midpoint standard	Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria are not appropriate for failed standards.	Sample results are not acceptable without a valid IS verification.
Method blank	One per preparatory batch	No analytes detected > ½ RL. and > 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results	Correct problem, then, If required, re-prep and reanalyze method blank and all samples processed with the contaminated blank.	Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Retention time window position establishment for each analyte	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA	NA	

Results reported between MDL and MRL	NA	NA	NA	Apply J-flag to all results between MDL and MRL.	

3.2.3 ANALYTICAL DATA QUALITY INDICATORS

The data quality indicators presented in this section are precision, accuracy (bias), representativeness, comparability, completeness, and sensitivity. Project-specific control limits for these indicators are presented in Table 2 Appendix C.

Precision. Precision is defined as the degree of agreement between or among independent, similar, or repeated measures. Precision is expressed in terms of analytical variability. For this project, analytical variability will be measured as the relative percent difference (RPD) or coefficient of variation between results between the primary and secondary determinations of water and SPME extractions. The precision goal for this project is 35%.

Precision will be calculated as the RPD as follows:

$$\%RPD_i = \frac{2|O_i - D_i|}{(O_i + D_i)} \times 100\%$$

where:

$\%RPD_i$	=	Relative percent difference for compound *i*
O_i	=	Value of compound *i* in original sample
D_i	=	Value of compound *i* in duplicate sample

The resultant RPD will be compared to acceptance criteria and deviations from specified limits reported. If the objective criteria are not met, the laboratory will supply a justification of why the acceptability limits were exceeded and implement the appropriate corrective actions. The RPD will be reviewed during data quality review, and deviations from the specified limits will be noted and the effect on reported data commented upon by the data reviewer.

Accuracy. Accuracy is the amount of agreement between a measured value and the true value. It will be measured as the percent recovery of standard samples versus the published value, verified by the secondary source verification standard.

Accuracy shall be calculated as percent recovery of target analytes as follows:

$$\%R_i = (Y_i \div X_i) \times 100\%$$

where:

$\%R_i$	=	percent recovery for compound *i*
Y_i	=	measured analyte concentration in sample *i* (measured - original sample concentration)
X_i	=	known analyte concentration in sample *i*

The resultant percent recoveries will be compared to acceptance criteria and deviations from specified limits will be reported. The second source verification standard limit is 25%. The accuracy limit is 35%. If the objective criteria are not met, the laboratory will supply a justification of why the acceptability limits were exceeded and implement the appropriate corrective actions. Percent recoveries will be reviewed during data quality review, and deviations from the specified limits will be noted and the effect on reported data commented upon by the data reviewer.

Representativeness. Representativeness is the degree to which sample results represent the system under study. In the present case, representativeness is addressed by the experimental design.

Comparability. Comparability is the degree to which data from one study can be compared with data from other similar studies, reference materials, and screening values. Comparability will be achieved through using standard techniques to collect and analyze representative samples and reporting analytical results in appropriate units.

Completeness. Completeness for usable data is defined as the percentage of usable data out of the total amount of planned data. The target goal for completeness is 95 percent for all data. Completeness for quality data shall be 95 percent for each individual analytical method. Quality data are data obtained in a sample batch for which all QC criteria were met. Completeness will be calculated as follows:

$$\%C = A / I \text{ x} 100\%$$

where:

$\%C$	=	Percent completeness (analytical)
A	=	Actual number of samples collected/valid analyses obtained
I	=	Intended number of samples/analyses requested

Non-valid data (i.e., data qualified as "R" rejected) will be identified during the QA review.

Sensitivity. The sensitivity of the analytical methods (i.e., method reporting limits) identified for this project are sufficient to allow comparison of project results to decision criteria. Analytical method reporting limits for all requested analytes are listed in Table 4.

3.3 Laboratory Equipment Maintenance

Laboratory instrumentation will be examined and tested prior to being put into service and will be maintained according to the manufacturer's instructions. Sampling personnel will maintain a supply of typical maintenance replacement items available in the field to help prevent downtime

because of equipment malfunctions. Examples of typical equipment maintenance items may include but not be limited sample containers and calibration standards.

All laboratory instruments will be maintained as specified in the project laboratory's QA plan and according to manufacturers' instructions. Manufacturer's instructions will be followed for any additional equipment that is required for the project.

3.4 Instrument Calibration

Laboratory instrument calibration will be conducted in accordance with the QC requirements identified in the manufacturers' instructions and the laboratory SOPs. General requirements are discussed below.

3.4.1 LABORATORY INSTRUMENTS

Calibration of all analytical instrumentation is required to ensure that the analytical system is operating correctly and functioning at the sensitivity required to meet project objectives. Each instrument will be calibrated with standard solutions appropriate to the instrument and analytical method, in accordance with the methodology specified and at the QC frequency specified in the laboratory SOPs (Provided in Appendix A).

The calibration and maintenance history of the fixed laboratory instrumentation is an important aspect of the project's overall QA/QC program. As such, all initial and continuing calibration procedures will be implemented by trained personnel following the manufacturer's instructions and in accordance with applicable EPA protocols to ensure the equipment is functioning within the tolerances established by the manufacturer and the method-specific analytical requirements.

3.4.2 STANDARD SOLUTIONS

A critical element in the generation of quality data is the purity/quality and traceability of the standard solutions and reagents used in the analytical operations. To ensure the highest purity possible, all primary reference standards and standard solutions will be obtained from a reliable commercial source. The laboratories will maintain a written record of the supplier, lot number, purity/concentration, receipt/preparation date, preparer's name, method of preparation, expiration date, and all other pertinent information for all standards, standard solutions, and individual standard preparation logs.

Standard solutions will be validated prior to use. Validation procedures can range from a check for chromatographic purity to verification of the concentration of the standard solution using another standard solution prepared at a different time or obtained from a different source. Stock and working standard solutions will be checked regularly for signs of deterioration, such as discoloration, formation of precipitates, or change of concentration. Care will be exercised in the proper storage and handling of standard solutions, and all containers will be labeled as to

compound, concentration, solvent, expiration date, and preparation data (initials of preparer/date of preparation). Reagents will be examined for purity by subjecting an aliquot or subsample to the corresponding analytical method as well.

3.5 Data Management

All project data and information must be documented in a format that is usable by project personnel in a manner that ensures data integrity, defensibility, and retrieval. The procedures describing how project data and information will be documented, tracked, and managed, from generation in the field to final use and storage are described in general below. Data will be generated by UT using manual notebooks and computers. The documentation report shall describe the UT:

- Team roles and responsibilities
- Data sources
  - Existing
  - New
- Software
  - Data conversion software used to import existing data
  - Data entry, review, and editing software
  - Analysis, modeling, and presentation software
- Hardware
- Documentation requirements
- Security procedures

Data will be provided to the Seattle District Corps of Engineers as a report and worksheet or database files. The Seattle District has a Data Management Program in place.

3.5.1 PROJECT DOCUMENTATION AND RECORDS

Project documents and records that will be generated for this project are described in the following sections.

Analytical Records

- Chain-of-custody records
- Sample receipt forms and sample tracking forms
- Preparation and analysis forms and/or logbooks
- Tabulated data summary forms and raw data for field samples, standards, QC checks, and QC samples
- Case narrative
- Sample chronology (time of receipt, extraction, and analysis)
- Identification of QC samples
- Communication logs
- Corrective action reports
- Definitions of laboratory qualifiers

- Documentation of corrective action results
- Documentation of laboratory method deviations
- Electronic data deliverables
- Instrument calibration reports
- Laboratory name
- Laboratory sample identification numbers
- Reporting forms, completed with actual results
- Signatures for laboratory sign-off (e.g., laboratory QA manager)
- Standards traceability records
- Other relevant project-specific documents in the laboratory's possession, such as telephone logs, MDL studies, initial precision and accuracy tests, and corrective action reports

Project Data Assessment Records

The following records will be retained by the Seattle District Project Manager or Technical Team Leader:

- Analytical audit checklists (when applicable)
- PT sample results (when applicable)
- Data review reports
- Telephone logs
- Corrective action reports
- Laboratory assessment (when applicable)
- Laboratory QA plan
- MDL study information

3.5.2 DATA PACKAGE DELIVERABLES

Results for fixed-based analyses will include the elements listed below:

- Case narrative
  - Airbills
  - Chain-of Custody Records (Traffic Reports)
  - Sample Tags
  - Sample Log-In Sheet
  - Miscellaneous Shipping/Receiving Record
  - Internal Lab. Sample Transfer Records and Tracking Sheets
- Sample Data:
  - Chromatograms from all columns for each sample
  - Other analytical raw data
- Standards Data:
  - Method Detection Limit Study Tabulated Summary Form
  - Initial Calibration Tabulated Summary

    - Continuing Calibration Tabulated Summary
    - Standards preparation logbook pages
- QC Data:
    - Surrogate Percent Recovery Tabulated Summary
    - Method Blank Tabulated Summary Form
    - Internal Standard Area and RT Tabulated Summary Form
    - QC Raw Data - chromatograms, quantitation reports, integration reports etc.
    - QC sample preparation logbook pages
- Miscellaneous Data:
    - Original preparation and analysis forms or copies of preparation and analysis logbook pages
    - Screening records (when applicable)
    - All instrument output, including strip charts, from screening activities (when applicable)
    - Preparation logs raw data
    - Other records (e.g., telephone communication log)

3.5.3 DATA REPORTING FORMATS

To ensure that project data are sufficient to meet both qualitative and quantitative DQO, laboratory data deliverables permitting a data quality assessment are required. Laboratory deliverables will be sufficient to permit a limited quality review of precision, accuracy, and adherence to the method SOP.

Information provided will be sufficient to review the data with respect to the following:

- Holding times and conditions
- Detection/quantitation limits\
- Initial and continuing calibration
- Laboratory Control Samples
- Precision and accuracy
- Representativeness
- Comparability
- Completeness

Fixed Laboratory Deliverables. The laboratory will prepare and retain full analytical and associated QC documentation. The laboratory will report the data along with associated QC reporting data. The final analytical data will be provided in a limited deliverable data format as described in this section.

The analytical results will be submitted to the USACE via hard copy and electronic files. The laboratory is responsible for ensuring that all EDD are free of errors and match the hard copy reports.

Hard Copy Deliverables. The laboratory will provide the following hard copy information for each analytical data package submitted for this project:

- The cover sheet will list the samples included in the report, provide narrative comments describing problems encountered in analysis, and identify any analyses not meeting QC criteria, including holding times.

- Chain of custody forms and cooler receipt forms will be provided.

- Detailed tabulated results will be provided in electronic form with inorganic and organic compounds identified and quantified, and reporting limits for all compounds and elements shown. All compounds and elements will be reported for each sample as a detected concentration or as not detected above the specific limits of quantitation, which must be stated. The laboratory will also report dilution factors, date of extraction, extraction batch number, date of analysis, and analytical batch number for each sample.

- Analytical results will be provided for QC sample spikes, laboratory duplicates, initial and continuing calibration verifications of standards and laboratory blanks, standard procedural blanks, LCS or equivalent, surrogates, laboratory reference materials, and detection limit check samples.

- Raw data system printouts (or legible photocopies) will be provided that identify date of reported analysis, analyst, parameters analyzed, calibration curves, calibration verifications, method blanks, any reported sample dilutions, cleanup logs, laboratory duplicates, spikes, control samples, sample spiking levels, preparation/extraction logs, run logs, and chromatograms.

- Chromatograms will be labeled with compound peaks, internal standards, and surrogate standards where applicable.

- The narrative accompanying the data package will include the identification of samples not meeting total QC criteria as specified in this QAPP, and/or the laboratory QA plans, and cautions regarding non-quantitative usability due to out-of-control QC results. Data reduction and QC review steps will be documented, signed, and dated by an authorized representative.

3.5.4 ELECTRONIC DATA MANAGEMENT

The USACE will use a relational database management system to track and report the following:

- Sample collection information including sample number, station, matrix, type of sample (field, blank, duplicate), date of collection, and sampler.

- Analytical results including concentration, units, qualifier and analytical method. Results shall also be provided in a format suitable for presentation in a report, with qualifiers indicated and associated descriptions included as footnotes where needed.

Laboratory electronic data deliverables will be directly loaded into the database management system, thereby avoiding hand-entry errors. After data quality review is performed, the changes in values or qualifiers will be incorporated into the project database by Seattle District. The project manager will provide additional information such as sampling date, location coordinates, and depth interval from field sampling documentation forms, which are added to the database.

4.0 Assessment and Oversight

4.1 Assessments and Response Actions

The ultimate responsibility for maintaining quality throughout the monitoring program rests with the USACE Project Manager. The day-to-day responsibility for ensuring the quality of the laboratory data rests with the Technical Team Lead, QA Manager, and the laboratory project manager or Principal Investigator.

Any non-conformances with the established QC procedures will be expeditiously identified and controlled. Where procedures are not in compliance with the established protocol, corrective actions will be taken immediately. Subsequent work that depends on the nonconforming activity will not be performed until the identified non-conformance is corrected.
No routine auditing is currently scheduled for this project. However, if problems are encountered that warrant further examination, performance and systems audits may be conducted to determine whether the following have occurred:

- The QA program has been documented in accordance with specified requirements.
- The documented program has been implemented.
- Any non-conformances were identified and corrective action or identified deficiencies were implemented.

4.1.1 PERFORMANCE AUDITS

Not applicable.

4.1.2 SYSTEMS AUDITS

No systems audits are proposed for this sampling and analysis sequence.

4.1.3 AUDIT PROCEDURES

No systems audits are proposed for this sampling and analysis sequence.

4.1.4 ASSESSMENT FINDINGS AND CORRECTIVE ACTION RESPONSES

The Technical Team Lead or designated representative will respond to the audit report within seven days of receipt. The response will clearly state the corrective action for each finding, including action to prevent recurrence and the date the corrective action will be completed. Follow-up action will be performed by the Technical Team Lead, QA Manager, or a designated representative to accomplish the following:

- Evaluate the adequacy of the USACE response

- Evaluate that corrective action is identified and scheduled for each finding
- Confirm that corrective action is accomplished as scheduled

Follow-up action may be accomplished through written communications, re audit, or other appropriate means. When all corrective actions have been verified, a memo will be sent to the USACE Project Manager and the EPA RPM signifying the satisfactory closeout of the audit.

Field Corrective Action.
Not applicable.

Laboratory Corrective Action. The laboratory QA data reviewer will review the data generated to ensure that all QC samples have been run as specified in the protocol. The following will be evaluated against the control limits listed in Appendix A: recoveries of LCSs and surrogates; and RPD for laboratory duplicates for consistency with method precision; and QC samples for analyses.
Laboratory personnel will be alerted that corrective actions are necessary if any of the following occur:

- The QC data are outside the warning or acceptance windows established for precision and accuracy. The laboratory PM will contact the laboratory QA manager to discuss out-of-control-limit data sets. If the analyses cannot produce data sets that are within control limits, the Technical Team Lead will be notified within 48 hours of any analysis that fails to meet the DQOs specified in this QAPP.
- Blanks contain contaminants at concentrations above the levels specified in the laboratory QA plan for any target compound.
- Undesirable trends are detected in LCS recoveries, RPDs or surrogate recoveries.
- Unusual changes in detection limits are observed.
- Deficiencies are detected by the laboratory QA manager during internal or external audits, or from the results of PE samples.

If any non-conformances in analytical methodologies or QC sample results are identified by the analyst, corrective actions will be implemented immediately. Specific corrective actions are outlined in each laboratory method SOP (see Appendix C) and the Quality Assurance Surveillance Plan (Appendix D). Corrective action procedures will be handled initially at the bench level by the analyst, who will review the preparation or extraction procedure for possible errors, check the instrument calibration, spike and calibration mixes, instrument sensitivity, etc. The analyst will immediately notify his/her supervisor of the identified problem and the investigation that is being conducted. If the problem persists or cannot be resolved, the matter will be referred to the laboratory supervisor and laboratory QA manager for further investigation. Once resolved, full documentation of the corrective action procedure will be filed by the laboratory QA manager in accordance with Appendix D.

.
Corrective actions may include, but will not be limited to the following:

- Reanalyzing suspect samples if holding time criteria permit.
- Re-exposing and analyzing new samples.
- Evaluating and amending sampling and/or analytical procedures (with USACE consultation).
- Accepting data with an acknowledged level of uncertainty (with USACE consultation).
- Recalibrating analytical instruments.
- Evaluating and attempting to identify limitations of the data

Data deemed unacceptable following the implementation of the required corrective action measures will not be accepted by the Technical Team Lead and follow-up corrective actions will be explored.

Corrective Actions Following Data Evaluation. The Technical Team Lead, or a designated party, will review the laboratory data generated for this project to ensure that all project QA objectives are met. If any non-conformances are found in the laboratory analytical and documentation procedures, and data evaluation and quality review procedures, the impact of those non-conformances on the overall project QA objectives will be assessed. Appropriate actions, including re-sampling and reanalysis, may be recommended in accordance with Appendix D, so that the project objectives can be accomplished. Any corrective actions required will be documented in a formal memorandum and submitted to the USACE PM.

4.1.4 AUDIT RECORDS

Original records generated for all audits will be retained in the central project files. Records will include audit reports, written replies, the record of completion of corrective actions, and documents associated with the conduct of audits that support audit findings and corrective actions as appropriate.

4.2 Final Project Reports

Field activities will be documented in a draft and final reports. The report will include the following:

- Summary of activities and identification of any deviations from this QAPP
- Tabulation of all laboratory data
- Descriptions of data analysis performed
- Interpretations of results in relation to the purpose and objectives of the project activities. This narrative will include a summary of study results and utility of SPME use quantitative measurements of compliance with surface water quality standards where such standards exist.

- Identification of areas where additional investigation may be needed
- Data quality review reports
- Data quality assessment summary

Forms, notes, and original laboratory data will be stored in the project files and will not be reproduced for these reports.

Draft reports will be submitted to EPA for review and comment. If necessary, a review conference may be held to discuss and clarify comments prior to production of the final reports.

5.0 Data Validation and Usability

5.1 Data Review, Verification, and Validation

The purpose of the data quality review is to eliminate unacceptable analytical data and to designate a data qualifier for any data quality limitation discovered. The data quality review will include a review of laboratory performance criteria and sample-specific criteria. The reviewer will determine whether the measurement quality objectives have been met, and will calculate the data completeness for the project.

Data quality reviews will be conducted by the UT, and confirmed by USACE Seattle District.

Data quality review consists of a review of the data summary forms that are generated for a set of data. At a minimum, chain-of-custody records, the case narrative, and the summary results for project samples and quality control samples are reviewed. The data are reviewed in accordance with the criteria contained in EPA guidance documents modified for the analytical method used.
The data quality review will include verification of the following:

- Compliance with this QAPP
- Proper sample collection and handling procedures
- Holding times
- QC results
- Instrument calibration verification
- Laboratory blank analysis
- Detection and MRL
- Laboratory duplicate precision
- Data completeness and format
- Data qualifiers assigned by the laboratory
- Surrogate compound recoveries
- Primary and secondary column verification
- Instrumentation calibration linearity

Qualifiers will be added to data during the review as necessary. Qualifiers applied to the data as a result of the review will be limited to:

U The analyte was analyzed for but was not detected above the reporting limit.

J The analyte was detected at a concentration less than the laboratory reporting limit, and the result is therefore considered an estimated quantity.

UJ The analyte was not detected above the sample reporting limit. However, the reporting limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

R The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified. No associated value is reported.

Results of the data quality review will be included in a data quality review report that will provide a basis for meaningful interpretation of the data quality and evaluate the need for corrective actions and/or comprehensive data validation.

5.1.1 DATA REVIEW PROCESS

The chemical data review process for this project will include data generation, data reduction, and two levels of QA review. The first level of QA review will be conducted by the laboratory prior to submittal of the electronic and hardcopy data to the USACE. After receipt of data packages, a data quality review will be performed in accordance with this QAPP.

Field Measurement Quality Assurance. The Technical Lead (Mandy Michalsen) is responsible for field quality assurance. She will review the deployment, retrieval and sample preparation documentation for consistency with established protocols. Field notes will be reviewed and checked for completeness and legibility. Where procedures are not strictly in compliance with established protocol, the deviations will be field documented and reported to the QA Manager. All corrective actions will be defined, documented, and implemented by the Technical Lead. A Quality Assurance Report will be filed for the field activity.

Laboratory Data Quality Assurance/Quality Control. Laboratory quality assurance will be reviewed by the laboratory according to the requirements in this QAPP, based upon the DOD QSM Version 4.1. A USACE data reviewer will verify all qualified data. The USACE data reviewer may edit a qualifier based on his or her professional judgment, which may include reviewing hardcopy data packages to resolve issues.

5.1.2 DATA INTERPRETATION

Site investigation results will be presented in text, tables, and graphics. Text will be in Microsoft Word format. Tabular data will be presented in Microsoft Excel format. Data will be exported from the project database to Excel for preparation of reports and other documents.

5.2 Reconciliation with User Requirements

Following the analyses, reporting, and data quality reviews have been completed, a data quality review report will be prepared. In this report, all data generated for this project will be reconciled with the project objectives.

References

Department of Defense (DOD). Quality Systems Manual for Environmental Laboratories, Version 4.1. 2006. http://www.navylabs.navy.mil/QSM%20Version%204.1.pdf

Mayer P, Vaes WHJ, Hermens JLM. 2000. Absorption of hydrophobic compounds into the poly(dimethylsiloxane) coating of solid-phase microextraction fibers: high partition coefficients and fluorescence microscopy images. Anal Chem 72: 459-464.

Pawliszyn, J. Solid phase microextraction, theory and application, 1996, Wiley-vch,Inc., NY,USA.

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste physical/chemical methods, 3rd ed. Method 3510C. SW-846. Office of Solid Waste and Emergency Response, Washington, DC.

Reible, D. G Lotufo, A Skwarksi, L Lampert, XiaoXia Lu. 2008. Laboratory Study Report, Demonstration and Evaluation of Solid Phase Microextraction for the Assessment of Bioavailability and Contaminant Mobility. ESTCP Project ER-0624. http://www.estcp.org/Technology/upload/ER-0624-Lab-Rep.pdf

Reible, D. (2010) Final Report on Calibration Study, April 26, 2010, University of Texas, Austin, TX 78712

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FIGURES

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Figure 1. Push-point sampler in the lab (upper) and insertion into intertidal sediment in the field (lower).

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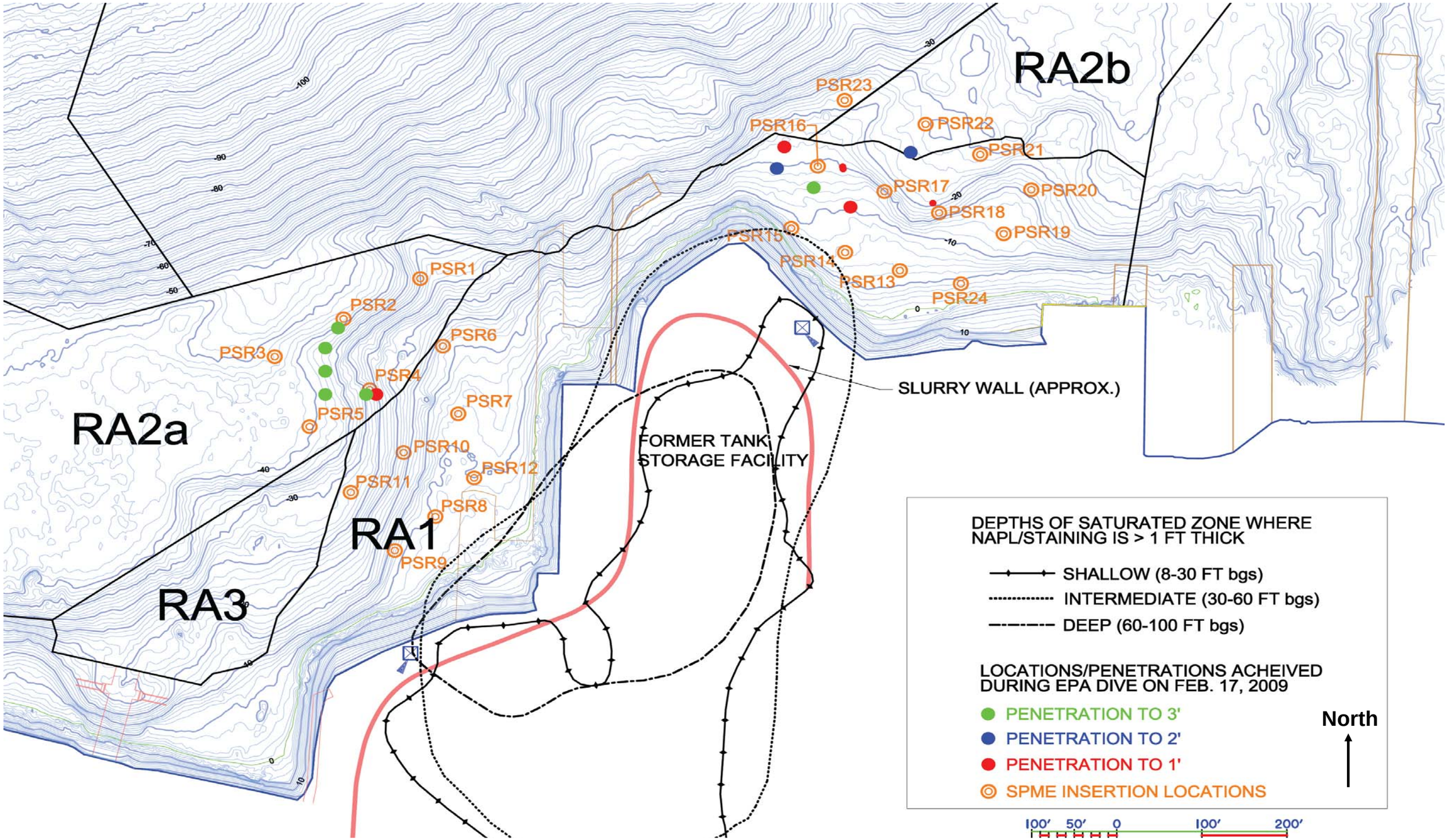

Figure 2. SPME sampling locations PSR1 – PSR24 shown in orange.

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Figure 3

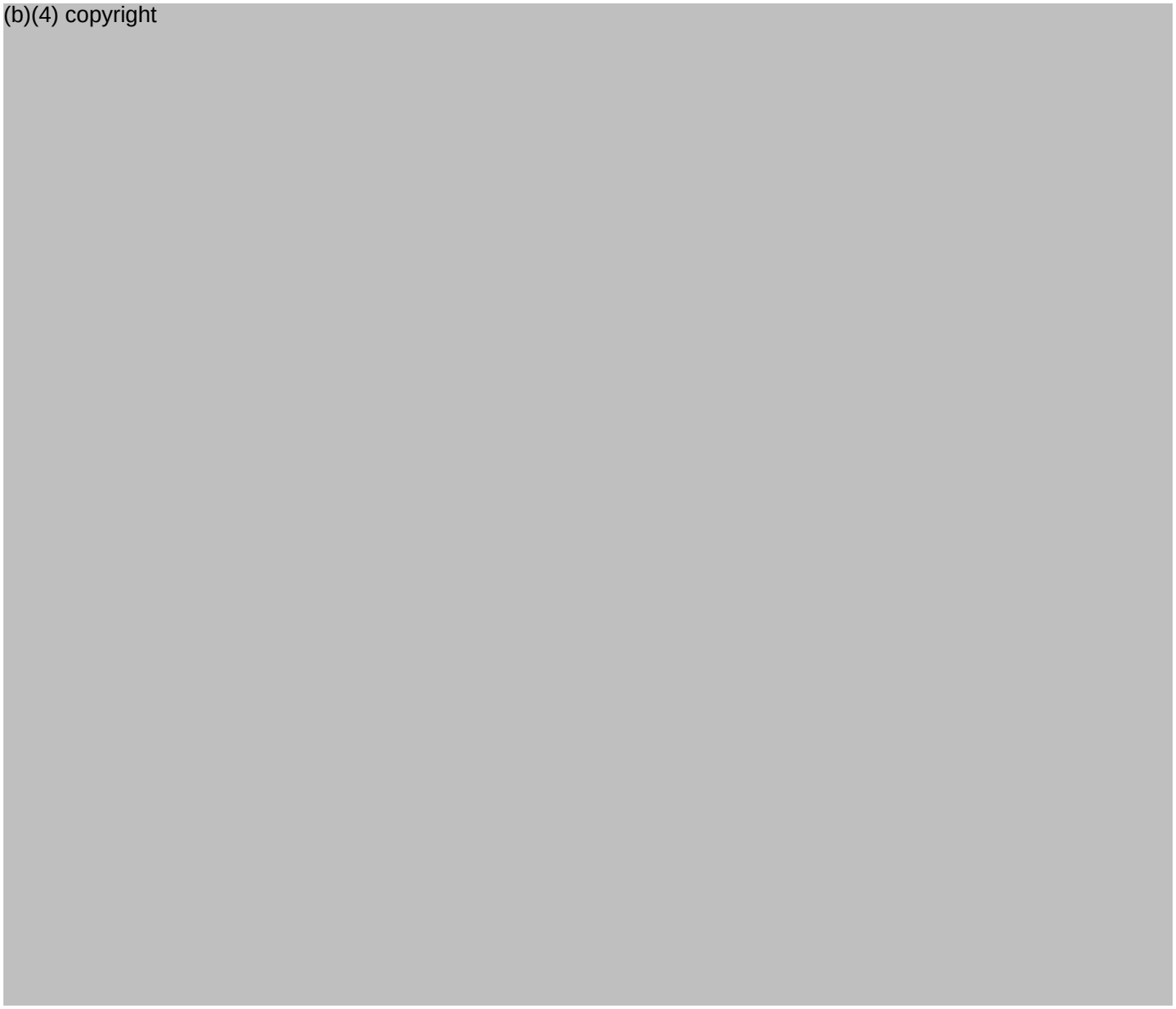

Figure 3. SPME background surface water sample will be deployed ~ 100 ft off of condo pilings.

Figure 4. Placement of the SPME fiber inside the push-point sampler.

APPENDIX A

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Environmental and Water Resources C1786 April 26, 2010
The University of Texas at Austin, Austin TX 78712
Bettie Margaret Smith Chair of Environmental Health Engineering
Phone: 512-471-4642 Email: reible@mail.utexas.edu

To: Mandy Michalsen, John Wakeman, Craig Martin
US Army Corps of Engineers

From: Danny Reible, PhD PE BCEE NAE

Re: Final Report Draft on Calibration Study

Summary of Results

A calibration study was conducted to accurately estimate fiber-water partition coefficients for polydimethylsiloxane (PDMS) as sorbent for PAHs in water collected at the Pacific Sound Resources Superfund site using a solid phase microextraction technique (SPME). The calibration was focused on the PAH_{16} compounds plus dibenzofuran and 2 methylnaphthylene. Acenaphthylene was excluded due to an inability to detect this compound at low concentrations via fluorescent detection. Benzo(g,h,i)perylene and indenopyrene were also treated as a single compound due to coelution under the high performance liquid chromatograpy (HPLC) conditions employed. A high and low concentration standard was prepared and diluted to generate 10 different concentration mixtures, 5 mixtures within each range. The low concentration range extended to near or below surface water quality standards while the high concentration range extended to near water solubility for individual compounds.

All compounds were detectable at concentrations below the surface water quality standard as indicated by both actual measurement or extrapolation of linear calibration curves using a single cm of a 230/210 PDMS SPME fiber (230 μm outside diameter with PDMS sheath and 210 μm glass core). The concentration magnification afforded by the fiber varied from a factor of 78.5 for naphthalene to 161,000 for benzo[g,h,i]perylene/indenopyrene. The lowest *measured* concentrations were below surface water quality criteria except for the combined benzo[g,h,i]perylene/indenopyrene concentration which was slightly higher than the surface water quality standard concentration for indenopyrene alone. Detectable concentrations for benzo[g,h,i]perylene/indenopyrene, as indicated by extrapolation of the linear calibration curve, were well below the surface water quality criteria (0.0063 μg/L vs 0.018 μg/L). Coefficient of variation at the lowest measured concentration (i.e. at or below the surface water quality standard) was less than 20% for all compounds except naphthalene and 2-methylnaphthylene. Most compounds exhibited a coefficient of variation at the lowest sample concentrations of less than 10% (i.e. equivalent to the variability in water measurements by conventional analytical techniques). Low range correlation coefficients for linear calibration of fiber-water partition coefficients exceeded 0.97 for all compounds except naphthalene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene/indenopyrene. Only naphthalene exhibited a correlation coefficient less than 0.9. Naphthalene measured by PDMS is subject to substantial errors due to the limited sample concentration magnification of naphthalene afforded by the sorbent and potential volatization losses during processing.

PDMS SPME sorption was also tested for high concentration range samples approaching the water solubility of the compounds. All compounds were introduced simultaneously into the test solutions and co-solvent effects apparently led to the formation of separate phases and inconsistent water concentrations at small dilutions of the high concentration standard with concentrations greater than 50% of solubility for any individual compound. Concentrations within approximately 5-10% of individual compound solubility were also observed to represent the maximum concentration that exhibited linear sorption onto the PDMS SPME fiber. At higher concentrations, the PDMS SPME fiber would be expected to provide only semi-quantitative concentration measurements. The high concentration range samples containing approximately 1-10% of the water solubility of the individual compounds were also fit to a linear calibration for fiber-water partition coefficient. Correlation coefficients were in excess of 0.93 for all compounds.

Introduction

Solid Phase Micro Extraction (SPME) is a demonstrated technology for measuring temporal and vertical contamination trends in sediment caps (Reible et al. 2008). However, there are site-related compounds at the Pacific Sound Resources (PSR) site that have not previously been extensively tested (calibrated) to the SPME and analytical instrumentation. This study is critical to verifying the use of this technology for use at multiple sites, but is being applied with particular attention to the Pacific Sound Resources' suite of contaminants and conditions, which may be generalized to multiple sites that have releases due to wood treatment residuals or other PAH sources.

The project goal is to develop accurate estimates of the fiber partition coefficients for SPME in known dissolved concentrations of the contaminants at the PSR site. The SPME sorbent material is the compound polydimethylsiloxane (PDMS), and the fiber partition coefficients relate to the mass of this sorbent. In previous SPME studies, semi-quantitative concentrations (i.e., relative to other field-measured concentrations) have generally been determined; however, the EPA requirement for the PSR site is to reliably relate porewater concentrations to thresholds (surface water quality standards).

The scope of work consists of preparing known concentrations of pure contaminants, exposing the SPME to these concentrations, and analyzing for recovery against the standard. The two ranges represent the concentrations near the surface water standards applicable to the site (low range), and high concentrations values that might be found should an active nearby source (e.g., a NAPL source or contaminated sediment lower in the sediment column) occur (high range). Together, the ranges will demonstrate the appropriateness and sensitivity of the SPMEs to these ranges of interest.

Project Background

At the PSR Superfund Site, creosote-related compounds remain in the subsurface and extend into the intertidal and subtidal regions of Elliott Bay in Puget Sound. These sediments have been capped during a prior remediation. During the current Five-Year Review (a Site requirement under the Comprehensive Environmental Restoration, Compensation, and Liabilities Act as amended), a significant data gap was identified relating to the potential for dissolved polynuclear aromatic hydrocarbons (PAHs) or non-aqueous phase liquids (NAPLs) to be released at water depths that would be logistically difficult to sample by conventional means (e.g., to 80 ft below Mean Lower Low Water). Accordingly, USEPA Region 10 has requested the Seattle District USACE to plan for and deploy a vertical-profiling SPME technology to determine the extent of creosote-related contamination in the sediment and capped sediments from that site.

The current effort is a necessary first phase of this work, namely, a laboratory calibration study to verify the capability of SPME technology for the intended purpose. Funding has been acquired for the current verification study from EPA Headquarters from an "Innovative Technologies" source.

Project Description

This calibration study measured the SPME method's ability for PDMS to adsorb polynuclear aromatic hydrocarbons (PAHs), as well as the compounds 2-methylnaphthalene and dibenzofuran, over a relevant range of freely-dissolved concentrations of the compounds in Puget Sound seawater. A series of water concentration standards (low range for near-criteria concentrations and high range for near solubility limit concentrations) were prepared. SPME with PDMS sorbent were placed in the water standards and allowed to equilibriate. Both water and PDMS SPME were then analyzed. Water concentrations were analyzed by direct injection into an HPLC (SW-846 Method 8310), where possible using either UV or fluorescence detection. When concentrations were too low for direct injection analysis, liquid-liquid extraction was employed to concentrate water samples. PDMS SPME fibers were analyzed by extraction directly into acetonitrile and direct injection of the solvent extract. Best fit

relationships between measured PDMS SPME concentration and water concentrations were determined as well as sorbent-water partition coefficients at each measured concentration. Linearity of the best fit relationships and constancy of measured sorbent-water partition coefficients were used as an indication of the ability to predict water concentration on the basis of measured PDMS SPME concentration. This report will summarize the efficacy of the SPME in quantifying the concentrations of these compounds over a range of concentrations. Project objectives, data gaps and investigation methods are summarized in Table 1 below.

TABLE 1 SUMMARY OF DATA QUALITY OBJECTIVES

Data Gap	Project Objectives	Investigation Methods	Performance Goal	Decision Criteria
Fiber (PDMS) coefficients over appropriate ranges for PAHs in water.	Assure that fiber coefficents are accurately characterized for PAHs, 2-methylnaphthlene, and dibenzofuran.	Provide a suitable range of concentrations in a controlled laboratory environment in site-relevant seawater; tumble SPMEs for a week, extract SPMEs, and perform regression analysis to determine partitioning relationship between SPMEs and known water concentrations.	Determine fiber coefficients in two concentration ranges of contaminants, and the error of the concentration estimates	The fiber coefficients should be reliable predictors of freely dissolved concentrations in the two ranges of interest: low (ambient water quality standards) and higher ("early warning" deep cap samples

Procedures

A low concentration standard (Std 1) and a high concentration standard (Std 2) were prepared and sequentially diluted with site surface water to generate a range of PAH concentrations in water. Target concentrations are listed in Appendix A. Actual concentrations were expected to vary from target concentrations due to the losses during handling and the relatively low stability of water –PAH mixtures. Actual concentration was measured in each diluted standard via either direct injection (at high concentrations) or liquid-liquid extraction (at low concentrations). Note that instrument calibration employs standards in solvent which are quite stable and less subject to losses during processing. Instrument calibration information can be found in Appendix B.

Three 1 cm fibers from Fiberguide Inc (NJ) containing polydimethylsiloxane (PDMS) in a 10 micron annulus on a 210 micron glass core (7 µL PDMS/m) were added to each bottle. $NaNO_3$ was added to prevent biodegradation of PAHs. The bottle was shaken for one week on a shaker at150 rpm. At the end of equilibration, the bottle was taken from the shaker table, three water samples were analyzed immediately by direct injection and three 300 ml water samples were analyzed by liquid-liquid extraction (extraction into dicholoromethane, sample concentration via blowdown and solvent exchange into acetonitrile). The three fibers were removed, blotted dry with tissue and extracted with 100 µL acetonitrile directly into autosampling vials for analysis. All analyses involved injection of 25 µL of sample (water for direct injection, acetonitrile for liquid-liquid extraction and PDMS) via SW-846 Method 8310. PAH detection was via UV for high concentrations and fluorescence for low concentrations. Calibration information, including second source standard calibration, of the UV and fluorescence detectors is summarized in

Appendix B. For fiber samples, the measured solvent concentration was converted to PDMS fiber equivalent concentration assuming that 100% of the PAHs on the equilibrated fiber were removed by extraction.
DOC content in site surface water was also measured via Method 5310B. The average DOC concentration in the collected water was 1.82 (±0.11 std. dev.) mg/L. At this DOC concentration, no significant influence of colloidal organic carbon is expected for any but the most hydrophobic PAHs as estimated by $C_{free\ water} = C_{total}/(1+DOC*K_{DOC})$. As DOC concentration increases and $DOC*K_{DOC}$ becomes significantly greater than 1, the effect of colloidal organic carbon increases. With a DOC concentration of less than 2 mg/L, a K_{DOC} in excess of $5x10^5$ L/kg is required before a majority of the contaminant is associated with colloidal organic carbon. This would typically require a compound with an octanol-water partition coefficient in excess of 10^6 [a]. Background PAH concentrations in site water and SPME fibers were also measured. PAHs were below detection limits in the site surface water. Analytical detection limits are also shown in Appendix B.

Quality assurance and quality control checks including laboratory control samples and calibration confirmation samples are summarized in Appendix C.

Analysis and Results

Low Concentration Range

Water concentrations were reported as µg PAH/L of water while fiber concentrations were reported as µg PAH/L of PDMS. The ratio of the two provides an estimate of the fiber water partition coefficient K_{fw}. Table 2 summarizes both measured water concentrations and the standard deviations of each measurement for the low range water concentrations. Note that low concentration range solutions were prepared from a 1:4000 dilution of the high concentration range standard rather than a 1:100 dilution of the low concentration standard to avoid any concerns about the solvent (methanol) concentration in the lesser dilution. Table 3 summarizes the measured fiber concentration for these low range water concentrations and Table 4 summarizes the effective fiber-water partition coefficient at each concentration.

Table 2 – Measured Water Concentrations- Low Concentration Range . Average of 3 replicates plus standard deviation (in red). Direct injection measurements in black and liquid-liquid extraction measurements in green.

[a] Burkhard LP. 2000. Estimating dissolved organic carbon partition coefficients for nonionic organic chemicals. Environ Sci Technol 34:4663-4668.

Low Concentration Range	std1 1:5000		std1 1:2000		std1 1:1000		std1 1:500		std1 1:100= std2 1:4000	
Water conc(µg/L)	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
Naphthalene	2.35	0.26	6.51	1.87	13.15	1.52	20.35	0.92	434.91	19.70
DBF	1.64	0.14	4.89	1.25	9.01	1.39	15.24	0.44	69.68	3.93
2-MNP	3.73	0.34	11.00	3.11	19.44	2.22	34.73	1.36	138.37	1.56
Fluorene	0.50	0.11	1.90	0.59	3.94	0.57	6.66	0.68	25.99	0.32
Acenaphthene	0.53	0.11	1.55	0.60	3.08	0.26	5.34	0.46	48.66	0.98
Phenanthrene	0.36	0.09	0.82	0.04	2.17	0.18	3.57	0.36	12.87	0.34
Anthracene	0.018	0.001	0.034	0.007	0.065	0.012	0.149	0.019	0.698	0.072
Fluoranthene	0.101	0.002	0.239	0.005	0.533	0.037	0.902	0.120	2.766	0.090
Pyrene	0.055	0.002	0.115	0.009	0.200	0.009	0.459	0.050	1.558	0.136
Chrysene	0.0012	0.0000	0.0024	0.0000	0.0046	0.0005	0.0090	0.0009	0.0550	0.0060
Benz[a]anthracene	0.0048	0.0000	0.0105	0.0005	0.0229	0.0044	0.0407	0.0029	0.1128	0.0074
Benzo[b]Fluoranthene	0.0009	0.0001	0.0015	0.0003	0.0027	0.0005	0.0065	0.0010	0.0158	0.0004
Benzo[k]Fluoranthene	0.0004	0.0000	0.0006	0.0000	0.0012	0.0002	0.0023	0.0003	0.0055	0.0002
Benzo[a]pyrene	0.0021	0.0002	0.0041	0.0005	0.0092	0.0018	0.0163	0.0013	0.0456	0.0017
Dibenz[a,h]anthracene	0.0090	0.0018	0.0139	0.0017	0.0332	0.0077	0.0585	0.0040	0.0024	0.0001
Benzo[ghi]+Indeno	0.0234	0.0079	0.0282	0.0018	0.0621	0.0141	0.1059	0.0071	0.0073	0.0004

Table 3 – Measured PDMS SPME fiber Concentrations- Low Concentration Range . Average of 3 replicates plus standard deviation (in red).

Low Concentration Range	std1 1:5000		std1 1:2000		std1 1:1000		std1 1:500		std1 1:100= std2 1:4000	
Fiber conc(µg/L)	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
Naphthalene	247	219	405	146	3619	938	927	812	55930	40775
DBF	5408	542	11567	1161	31809	5872	58157	13283	445305	33711
2-MNP	3256	2287	4811	922	26929	11464	30905	16903	339257	83168
Fluorene	2480	138	5762	515	14586	2205	30085	8603	108960	7449
Acenaphthene	1291	182	2816	422	8559	1571	14856	4229	175734	13842
Phenanthrene	2795	35	7174	662	15917	1861	32880	5938	137871	4606
Anthracene	190		443	80	938	62	1951	186	7651	523
Fluoranthene	2379	236	6645	1579	12429	1235	25394	2830	82611	2832
Pyrene	1268	103	3573	386	7345	1049	14302	1902	54760	1240
Chrysene	89	17	228	16	373	88	695	124	3010	75
Benz[a]anthracene	352	14	1107	115	1985	293	3847	487	9646	274
Benzo[b]Fluoranthene	99	11	238	49	461	113	801	119	1948	118
Benzo[k]Fluoranthene	42	3	119	13	222	40	364	48	682	40
Benzo[a]pyrene	357	21	992	85	1849	293	2997	391	5953	325
Dibenz[a,h]anthracene	1396	77	3874	316	6703	1066	9023	1921	264	75
Benzo[ghi]+Indeno	2532	178	7180	590	12376	2112	17328	3419	786	68

Table 4 – Effective PDMS SPME fiber-water partition coefficient – Low Concentration Range plus average, standard deviation and coefficient of variation (standard deviation divided by average) in %.

Low Concentration Range								
K_{f-w}	std1 1:5000	1:2000	1:1000	1:500	std1 1:100= std2 1:4000	average	stdev	COV (%)
Naphthalene	105	62	275	46	129	123	91	74
DBF	3293	2365	3532	3816	6391	3879	1506	39
2-MNP	873	437	1385	890	2452	1207	772	64
Fluorene	4930	3028	3699	4517	4192	4073	738	18
Acenaphthene	2453	1820	2783	2783	3612	2690	648	24
Phenanthrene	7731	8764	7323	9213	10710	8748	1335	15
Anthracene	10290	13047	14413	13136	10968	12371	1697	14
Fluoranthene	23597	27811	23317	28140	29867	26546	2928	11
Pyrene	23140	31099	36705	31157	35141	31448	5256	17
Chrysene	76190	94181	81358	77340	54711	76756	14243	19
Benz[a]anthracene	73328	105377	86752	94522	85539	89104	11846	13
Benzo[b]Fluoranthene	110892	162914	172010	123845	123258	138584	27057	20
Benzo[k]Fluoranthene	106828	183790	181224	157684	124677	150840	34195	23
Benzo[a]pyrene	166060	241838	201921	183504	130440	184753	41395	22
Dibenz[a,h]anthracene	155012	278758	201735	154228	111114	197433	58590	30
Benzo[ghi]+Indeno	108283	254586	199383	163689	107897	181485	61480	34

The coefficient of variation in the average fiber-water partition coefficient gives an indication of the linearity between PAH concentration and sorption onto the fiber (or alternatively the constantcy of the fiber-water partition coefficient. The fiber-water partition coefficient is effectively constant, and there exists a good linear relationship (<25% coefficient of variation) between PAH concentration and sorption onto the fiber for all compounds except the three least hydrophobic naphthalene, dibenzofuran and 2 methylnaphthalene, and the two most hydrophobic compounds, dibenzo[a,h) anthracene and benzo(g,h,i)perylene/indenopyrene. The variation in dibenzofuran is driven by a single outlier concentration at the least diluted standard.

An alternative means of evaluating the linearity between sorption onto the PDMS SPME fiber and water concentration is to conduct a linear regression on the data. Best fit relationships between low range water concentrations and equilibrium fiber concentration are shown in Appendix D for all compounds. The slope of this relationship is the fiber-water partition coefficient, K_{fw} or a concentration magnification factor. Table 5 summarizes the best-fit fiber-water partition coefficients and the correlation coefficient of the fit. The fiber-water partition coefficient varies from 78.5 to 161,000 and the correlation coefficients are generally above 0.99. The most hydrophobic compounds have slightly weaker fits and naphthalene has a very low correlation coefficient. Naphthalene measured by PDMS is subject to substantial errors due to the limited sample concentration magnification of naphthalene afforded by the sorbent and potential volatization losses during processing.

Table 5 – Summary of linear correlation between measured water and PDMS fiber concentrations. Also included is minimum measured concentration and coefficient of variation in both fiber and water at that concentration. Also included is the concentration that is effectively indistinguishable from zero on the basis of the best fit linear correlation (based upon the correlation intercept). The theoretical detection limit for a 1 cm length of PDMS fiber is also included based upon calculation from the direct water injection MDL from Table B3. The surface water quality concentration, the desired low concentration endpoint is also included for comparison and the maximum concentration used in fitting the fiber-water partition coefficient.

	Low Range K_{fw}	Low Range r^2	Low Range Min Conc µg/L	COV % Fiber Lowest Conc.	COV % Water Lowest Conc	Low Conc ~ 0 (linear fit) µg/L	Fiber MDL µg/L *	Surface Water Quality Std µg/L	Low Range Max Conc µg/L
Naphthalene	78.5	0.1547	2.35	88.8%	11.0%	5.96	0.3332	9.58	435
DBF	4027	0.985	1.64	10.0%	8.5%	1.06	0.0123		70
2-MNP	2591	0.9817	3.73	70.2%	9.2%	10.19	0.0268		138
Fluorene	4227	0.9984	0.503	5.6%	21.7%	0.14	0.0697	3460	26
Acenaphthene	3662	0.9996	0.526	14.1%	20.0%	0.73	0.0315	640	49
Phenanthrene	10938	0.9973	0.362	1.3%	25.5%	0.36	0.0076		13
Anthracene	10810	0.998	0.018	18.1%	6.9%	0.014	0.0075	26400	0.7
Fluoranthene	30327	0.9985	0.101	9.9%	2.2%	0.054	0.0025	90	2.77
Pyrene	35394	0.9987	0.055	8.1%	3.8%	0.018	0.0021	2590	1.56
Chrysene	52898	0.9967	0.0012	19.1%	1.5%	0.0022	0.00048	0.018	0.055
Benz[a]anth	85097	0.9978	0.0048	3.9%	0.1%	0.0015	0.00011	0.018	0.112
Benzo[b]F	119712	0.9945	0.00089	11.6%	11.5%	0.00047	0.00011	0.018	0.0158
Benzo[k]F	120458	0.9781	0.00039	8.0%	1.4%	0.00036	0.00002	0.018	0.0055
Benzo[a]pyrene	122795	0.9755	0.0021	5.8%	7.5%	0.00431	0.00005	0.018	0.046
Dibenz[a,h]anthracene	142042	0.9241	0.009	5.5%	19.5%	0.00829	0.00007	0.018	0.059
Benzo[ghi]perylene + Indenopyrene	161013	0.9179	0.0234	7.0%	34.0%	0.00632	0.00010	0.018	0.106

Fiber MDL = MDL (Table B3)(25µL injection volume)/(K_{fw}*0.069 µL PDMS/cm)

Also included in Table 5 is the lowest measured concentration and the coefficient of variation at the lowest concentration based upon the three triplicate samples for both PDMS SPME fiber and water. For most compounds, the coefficient of variation in the PDMS SPME fiber measurement is similar to or less than the coefficient of variation in the water measurement by conventional means. Only naphthalene and 2-methylnaphthalene exhibit coefficients of variation at the lowest concentration that are substantially higher due to the difficulties of measuring low hydrophibicity compounds with PDMS SPME.

Also included in Table 5 is the predicted concentration that is indistinguishable from zero concentration based upon the best-fit intercept of the linear correlation. The estimate is the best-fit intercept divided by the slope (or fiber-water partition coefficient) and indicates the concentration that corresponds to the best-fit intercept. This is generally a conservative indicator of detection limit (and in fact many of the lowest measured concentrations are less than this intercept). The theoretical detection limit, fiber MDL, is the water concentration that would lead to a PDMS fiber concentration detectable at the MDL by direct water injection in the HPLC (last column of Table B3). This is calculated by

$$C_{f-MDL} = \frac{C_{MDL}(25\mu L\, injection\, volume)}{K_{fw}(PDMS\, volume)}$$

Where C_{f-MDL} is the PDMS MDL, C_{MDL} is the direct injection water concentration from Table B3, K_{fw} is the PDMS fiber-water partition coefficient (second column Table 5) and the PDMS volume is the volume extracted into a single injection (in this case, 1 cm of a 10 µm PDMS layer on a 210 µm core or 0.069 µL PDMS). Routine quantification is likely expected at a concentration approximately 10 times this concentration. For comparison purposes, the targeted lower concentration, the surface water quality standard is also included in Table 5 as well as the highest concentration used in the fitting for the low concentration range.

A review of the information in Tables 2-5 indicates that the PDMS SPME was able to accurately measure water concentrations at concentrations below the surface water quality concentrations of concern. There is greater uncertainty with the least hydrophobic compounds for which PDMS does not provide as great a magnification effect

and which can evaporate from both aqueous solutions and the PDMS fibers. In general, however, the PAHs can be detected accurately and at low concentrations.

High Concentration Range

In the high concentration range, a more limited range of concentrations are available for evaluation of PDMS SPME. At the lowest dilutions of standard 2 (the high concentration standard) (1:200 and 1:100 dilution), concentration results were inconsistent with the dilutions. For the 1:100 dilution in particular, the water solution looked cloudy and concentrations, especially for the more hydrophobic compounds, are significantly greater than their solubility. This was likely the result of the difficulty of achieving full dissolution of the PAHs at the high concentrations, resulting in inconsistent measurements. The mixture of multiple PAHs, as well as solvent from the dilution standard, may have led to an effective solubility different from that reported for individual compounds.

Table 6 shows the water concentration measured in the various dilutions in the high concentration standard. The associated SPME concentrations and fiber-water partition coefficients in the high concentration range are shown in Figures 7 and 8, respectively.

Table 6 – Measured Water Concentrations- High Concentration Range . Average of 3 replicates plus standard deviation (in red). Direct injection measurements in black and liquid-liquid extraction measurements in green.

High Concentration Range	std2 1:2000		std2 1:1000		std2 1:500		std2 1:200		std2 1:100	
Water conc(µg/L)	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
Naphthalene	1108.45	59.85	2002.46	50.85	4166.59	749.15	8630.65	106.90	22280.38	5593.34
DBF	288.78	25.93	471.23	38.35	1017.78	183.53	2050.70	38.61	28439.41	5880.35
2-MNP	604.67	46.99	1051.40	16.37	2238.49	406.89	4529.36	71.16	44954.34	11522.48
Fluorene	66.13	4.18	114.80	1.87	247.30	42.70	461.00	6.84	7166.47	1596.77
Acenaphthene	137.24	10.45	253.73	37.68	548.64	95.07	979.16	50.35	14156.45	4826.59
Phenanthrene	35.02	1.92	51.93	1.13	129.02	24.19	248.41	4.91	5106.13	1446.33
Anthracene	1.98	0.09	2.60	0.20	5.06	0.87	8.40	0.35	252.29	81.25
Fluoranthene	7.22	0.31	12.96	0.26	30.42	4.53	54.62	0.23	1291.98	414.83
Pyrene	4.05	0.55	7.55	0.22	17.52	2.45	34.20	0.75	717.68	241.97
Chrysene	0.1015	0.0166	0.1977	0.0585	0.3637	0.0567	0.5691	0.3978	13.1390	3.6413
Benz[a]anthracene	0.2724	0.0258	0.4815	0.0102	1.1155	0.1915	1.9177	0.1117	43.8715	5.5727
Benzo[b]Fluoranthene	0.0377	0.0038	0.0725	0.0094	0.1555	0.0319	0.2735	0.0926	6.5753	1.8894
Benzo[k]Fluoranthene	0.0102	0.0007	0.0223	0.0021	0.0511	0.0084	0.0975	0.0532	2.8363	0.8666
Benzo[a]pyrene	0.1033	0.0052	0.1838	0.0029	0.4882	0.0856	0.8961	0.0110	23.5025	7.1129
Dibenz[a,h]anthracene	0.0044	0.0003	0.0067	0.0005	0.0207	0.0018	0.0602	0.0633	69.7632	3.5435
Benzo[ghi]+Indeno	0.0141	0.0011	0.0195	0.0028	0.0584	0.0037	0.1367	0.0352	128.5389	5.5001

Table 7 – Measured PDMS SPME fiber Concentrations- High Concentration Range . Average of 3 replicates plus standard deviation (in red).

High Concentration Range	std2 1:2000		std2 1:1000		std2 1:500		std2 1:200		std2 1:100	
Fiber conc(µg/L)	average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
Naphthalene	182793	123575	297862	197884	1512208	983727	3738759	1539796	27770597	5499014
DBF	976869	92734	2053231	191618	5031291	471242	23727873	5840387	82846789	15265473
2-MNP	853703	233929	1659906	531744	5416910	1711548	17080533	6376717	80439711	3305216
Fluorene	278080	19634	598937	51439	1507396	110805	8652378	2252714	28468068	6722338
Acenaphthene	592110	128744	983803	19498	2341020	265903	12411151	4590316	33985411	12854493
Phenanthrene	278631	13469	611978	54141	1469968	80869	6388929	1158506	10114168	1338879
Anthracene	17614	1514	33476	2671	94133	9595	667317	274060	1017475	200193
Fluoranthene	165620	5668	357838	21004	900006	31892	2874628	292530	1639451	127461
Pyrene	107846	5700	228871	8348	591738	12530	1861314	227959	968756	69684
Chrysene	6415	85	11049	951	29557	3233	42238	5635	18192	3604
Benz[a]anthracene	21560	746	36565	8381	92034	3529	130489	17496	53796	5041
Benzo[b]Fluoranthene	4756	62	6732	3695	13728	1339	7859	1209	5865	1061
Benzo[k]Fluoranthene	1712	38	2355	1370	4839	482	2773	372	2181	244
Benzo[a]pyrene	13507	245	19153	10916	41033	3715	22761	2924	19165	1700
Dibenz[a,h]anthracene	690	54	638	535	937	161	504	242	1002	234
Benzo[ghi]+Indeno	1785	24	1906	1511	2786	575	1438	232	2958	1149

Table 8 – Effective PDMS SPME fiber-water partition coefficient – High Concentration Range plus average, standard deviation and coefficient of variation (standard deviation divided by average) in %. Also included is student t test of whether the estimated fiber-water partition coefficient in the high concentration range is

significantly different from the fiber-water partition coefficient in the low concentration range. Values of $p<0.05$ indicate that the results are significantly different in the two concentration ranges.

$K_{f\text{-}w}$	std2 1:2000	1:1000	1:500	1:200*	1:100*	average 500-2000 dilutions	stdev	COV (%)	p value
Naphthalene	165	149	363	433	1246	226	119	53	0.29
DBF	3383	4357	4943	11571	2913	4228	788	19	0.15
2-MNP	1412	1579	2420	3771	1789	1804	540	30	0.25
Fluorene	4205	5217	6095	18769	3972	5172	946	18	0.18
Acenaphthene	4314	3877	4267	12675	2401	4153	240	6	0.006
Phenanthrene	7956	11785	11394	25719	1981	10378	2107	20	0.315
Anthracene	8905	12896	18608	79442	4033	13470	4877	36	0.74
Fluoranthene	22931	27610	29588	52632	1269	26709	3419	13	0.95
Pyrene	26625	30320	33770	54420	1350	30238	3574	12	0.71
Chrysene	63230	55878	81259	74215	1385	66789	13059	20	0.36
Benz[a]anthracene	79141	75942	82501	68043	1226	79195	3280	4	0.14
Benzo[b]Fluoranthene	126141	92889	88273	28736	892	102434	20660	20	0.09
Benzo[k]Fluoranthene	167201	105536	94602	28443	769	122446	39143	32	0.36
Benzo[a]pyrene	130800	104190	84044	25401	815	106345	23452	22	0.01
Dibenz[a,h]anthracene	156620	94697	45344	8371	14				
Benzo[ghi]+Indeno	126238	97562	47724	10519	23				
	* Not included in averages								

The average fiber-water partition coefficient in Table 8 excludes both the 1:100 standard 2 dilution (indicated previously as exhibiting separate phase behavior) and the 1:200 standard 2 dilution. The elimination of the 1:200 dilution is the result of the fact that the fiber concentrations and the fiber-water partition coefficients are not linear in this concentration range. The concentrations in the 1:200 dilution are typically approximately 25% of the individual compound solubilities. The deviation from linearity could be the result of separate phase behavior in the solution due to the mixture of compounds and solvent although the water concentrations in Table 6 do not indicate that behavior. It is also possible that sorption to the PDMS is nonlinear at these high concentrations. Because of the deviation from linearity, however, the averages in Table 8 reflect only the 3 dilutions 1:2000, 1:1000 and 1:500 and extend up to a concentration that is approximately 5-10% of the individual compound solubility. The coefficient of variations of the fiber-water partition coefficients are generally good although somewhat higher, in general, than for the low concentration range partition coefficients. Also included in Table 8 is a test of whether the fiber-water partition coefficient at high concentration is statistically different from the low concentration range partition coefficient. If the p value is less than 0.05 then it is statistically likely that the fiber-water partition coefficient is different in the high concentration range. Only benzo(a)pyrene and acenaphthene meet this statistical test. Any differences in the other compounds between the fiber-water partition coefficient at high and low concentrations are not statistically significant.

Table 9 summarizes the best-fit fiber-water partition coefficients and the correlation coefficient of the fit in the high concentration range. The fiber-water partition coefficient varies from 78.5 to

161,000 and the correlation coefficients are generally above 0.99. The most hydrophobic compounds have slightly weaker fits and naphthalene has a very low correlation coefficient. Naphthalene measured by PDMS is subject to substantial errors due to the limited sample concentration magnification of naphthalene afforded by the sorbent and potential volatization losses during processing.

Table 9 – Summary of linear correlation between measured water and PDMS fiber concentrations. Also included is minimum and maximum measured concentration used to create the fit. The maximum concentration is also compared to the solubility of the individual PAH compound.

	High Range K_{fw}	High Range r^2	High Range Min Conc µg/L	High Range Max Conc µg/L	Sol ug/L
Naphthalene	401	0.9337	1108	4167	31000
DBF	5536	0.9997	289	1020	3100
2-MNP	2869	0.9897	605	2238	24600
Fluorene	6800	0.9999	66	247	1690
Acenaphthene	4320	0.996	137	549	3900
Phenanthrene	12199	0.989	35	129	1150
Anthracene	24777	1	1.98	5.06	43.4
Fluoranthene	31519	0.9998	7.22	30.4	260
Pyrene	36021	0.9999	4.05	17.5	430
Chrysene	90781	0.9676	0.101	0.364	3.45
Benz[a]anth	84494	0.9986	0.272	1.116	9.4
Benzo[b]F	77630	0.9936	0.038	0.156	1.5
Benzo[k]F	78206	0.9909	0.01	0.051	0.8
Benzo[a]pyrene	71606	1	0.103	0.488	9.4
Dibenz[a,h]anthracene					2.49
Benzo[ghi]perylene + Indenopyrene					0.26/1.76

A review of the information in Tables 6-9 indicates that the PDMS SPME was also able to accurately measure water concentrations in the high concentration range. Accurate measurement assuming a linear model should be limited to concentrations less than 10% of the individual compound solubility, at least in the tested mixture. In general the fiber-water partition coefficients are not substantially different in the low or high concentration ranges. Extrapolation to higher concentrations, however, would be expected to be only semi-quantitative. Thus the PDMS SPME could be used for indicating potential source areas as an early warning indicator of contaminant migration but that at high concentrations, absolute concentration measurements may not be as accurate as at lower concentrations

Fiber-water Partition Coefficient- correlation with K_{ow}

All compounds except naphthalene, 2-MNP, dibenz[ah]anthracene and benzo[g,h,i]perylene/indeno[1,2,3-cd]pyrene were used to identify a correlation between the fiber-water partition coefficient, K_{fw}, and the hydrophobicity of the compound as measured by the octanol-water partition coefficient, K_{ow}. The result is the correlation

$$\text{Log } K_{fw} = 0.839 \text{ Log } K_{ow} + 0.117 \qquad (R^2=0.971)$$

The predicted K_{fw} and the error between the predicted and observed values are also shown in Table 10. The correlation can be used to predict fiber-water partition coefficients when experiment measurements are unavailable.

Table 10 - Summary of calibration fits between water concentration and fiber- water partition coefficients (*K*fw). Correlation (0.799 Log Kow +0.173) fit includes all data.

	Low Range K_{fw}	Log K_{fw}	Log K_{ow}	predicted Log K_{fw}	Error
Naphthalene	78.5	1.89	3.37	2.86	51.2%
DBF	4027	3.60	4.3	3.61	0.1%
2-MNP	2591	3.41	3.9	3.29	-3.7%
Fluorene	4227	3.63	4.18	3.51	-3.2%
Acenaphthene	3662	3.56	3.92	3.30	-7.3%
Phenanthrene	10938	4.04	4.57	3.82	-5.3%
Anthracene	10810	4.03	4.54	3.80	-5.8%
Fluoranthene	30327	4.48	5.22	4.34	-3.1%
Pyrene	35394	4.55	5.18	4.31	-5.2%
Chrysene	52898	4.72	5.86	4.85	2.7%
Benz[a]anth	85097	4.93	5.91	4.89	-0.7%
Benzo[b]F	119712	5.08	5.8	4.81	-5.4%
Benzo[k]F	120458	5.08	6	4.97	-2.3%
Benzo[a]pyrene	122795	5.09	6.04	5.00	-1.8%
Dibenz[a,h]anthracene	142042	5.15	6.75	5.56	8.0%
Benzo[ghi]perylene + Indenopyrene	161013	5.21	6.72	5.54	6.4%

Appendix A Target Calibration Concentrations

Table A1 . Experimental Design for Standards Series

Series	Surface Water Quality Standards	1	2	3	4	5	Low Standard	6	7	8	9	10	High Standard	Note
	µg/L	5000	2000	1000	500	100	ug/L	2000	1000	500	200	100	ug/L	
Acenapthene	640	0.4	1	2	4	20	**2000**	98.25	196.5	*393*	*982.5*	1965	**196500**	
Anthracene	26,400	0.01475	0.036875	0.07375	0.1475	0.7375	**73.75**	1.475	2.95	5.9	14.75	29.5	**2950**	1
Benzo(a)anthracene	0.018	0.0036	*0.009*	0.018	*0.036*	0.18	**18**	0.3	0.6	1.2	3	6	**600**	
Benzo(a)pyrene	0.018	0.00095	0.002375	0.00475	*0.0095*	*0.0475*	**4.75**	0.095	0.19	0.38	0.95	1.9	**190**	
Benzo(b)fluoranthene	0.018	0.0003	0.00075	0.0015	0.003	*0.015*	**1.5**	*0.03*	0.06	0.12	0.3	0.6	**60**	
Benzo(k)fluoranthene	0.018	0.000138	0.000344	0.000688	0.00138	0.0069	**0.6875**	*0.01375*	*0.0275*	0.055	0.1375	0.275	**27.5**	
Benzo(g,h,i)perylene	n/a	0.00013	0.000325	0.00065	0.0013	0.0065	**0.65**	0.0065	*0.013*	*0.026*	0.065	0.13	**13**	2
Chrysene	0.018	0.000818	0.002044	0.004088	*0.00818*	*0.0409*	**4.0875**	0.08175	0.1635	0.327	0.8175	1.635	**163.5**	
Dibenz(a,h)anthracene	0.018	0.000125	0.000313	0.000625	0.00125	0.0063	**0.625**	*0.0125*	*0.025*	0.05	0.125	0.25	**25**	
Fluoranthene	90	0.05825	0.145625	0.29125	0.5825	2.9125	**291.25**	5.825	11.65	23.3	*58.25*	*116.5*	**11650**	
Fluorene	3,460	0.4	1	2	4	20	**2000**	46	92	184	460	920	**92000**	1
Indeno (1,2,3-cd) pyrene	0.018	0.002	0.005	*0.01*	0.02	*0.1*	**10**	1.55	3.1	6.2	15.5	31	**3100**	
Naphthalene	9.58	1.916	*4.79*	*9.58*	19.16	95.8	**9580**	797.5	1595	3190	7975	15950	**1595000**	
Pyrene	2,590	0.0335	0.08375	0.1675	0.335	1.675	**167.5**	3.35	6.7	13.4	33.5	67	**6700**	1
Phenanthrene	n/a	0.2725	0.68125	1.3625	2.725	13.625	**1362.5**	27.25	54.5	109	272.5	545	**54500**	2
2-Methylnaphthalene	n/a	6.25	15.625	31.25	62.5	312.5	**31250**	625	1250	2500	6250	12500	**1250000**	2
Dibenzofuran	n/a	2.5	6.25	12.5	25	125	**12500**	250	500	1000	2500	5000	**500000**	2

Italics indicate the bracketing concentrations with respect to the ambient water quality standards. Where there is only one value highlighted [Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, Dibenz(a,h)anthracene, and Indeno(1,2,3-cd)pyrene] the surface water quality standard, 0.018 ug/L, was selected as the target detection limit. This value was determined to be achievable by liquid-liquid extraction (it is 11x lower than that achievable by direct injection.

Blue highlighting indicates values that are believed to be either below the achievable Method Detection Limit or are "out of critical range" for the low calibration series. Because all values in the dilution series 1 are highlighted, these series have been been eliminated from the design.

Note 1. Water quality standard is near solubility limit. A range below the standard was selected.
Note 2. No water quality standard identified.

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Appendix B Instrument Calibration

Detector calibration

The calibration standard was obtained from Ultra Scientific Inc, the standard contains 16 PAHs with identical concentrations of each compound. The calibration results are listed in the following table.

Table B1 Initial calibration for 16 PAHs by HPLC

Fluorescence Detector

	Conc(µg/L)	100	50	20	5	1	0.5	0.1	0.05		
Compounds	**RT**									RPF	R2
Naphthalene	7.261		772187	303133	78309	16039	10184			6.49E-05	0.9998
Fluorene	9.865	584817	299832	123963	58810	17181	18583			1.69E-04	0.9951
Acenaphthene	10.246	1125791	564941	226889	57478	14674	8783			8.87E-05	1.0000
Phenanthrene	10.729		1089099	436403	116294	26141	13046			4.58E-05	0.9999
Anthracene	11.428	432855	222725	85531	19495	4252	2213			2.30E-04	0.9997
Fluoranthene	13.247	529688	275725	105796	23307	5676	3240			1.87E-04	0.9995
Pyrene	14.325	972010	489590	191975	45821	8207	5010			1.03E-04	0.9998
Chrysene	17.505		1362220	526081	125453	30175	12729	1796	1681	3.69E-05	0.9997
Benz[a]anth	18.044		3071978	1518494	361729	77527	36666	6430	4007	1.32E-05	0.9997
Benzo[b]	23.221		2430460	952055	203177	50078	24180	4499	3391	2.07E-05	0.9993
Benzo[k]	24.105				2175510	471678	222520	43062	24272	2.29E-06	0.9996
Benzo[a]pyr	25.339		4338071	2134057	481956	107733	51596	10159	5372	9.42E-06	0.9993
Dibenz[a,h]	30.483		2251274	879563	213342	44123	20477	5193	1966	2.29E-05	0.9995
Benzo[ghi]+Indeno	33.685		3414901	1396091	336018	103540	33186	5977	3509	2.92E-05	0.9998

RSF=standard concentration/peak area

	Conc(µg/L)	100	50	20	5	1	0.5	0.1	0.05	mean RSF	RSD(%)
Compounds											
Naphthalene			6.475E-05	6.6E-05	6.385E-05	6.235E-05	4.91E-05			6.12E-05	11.2685
Fluorene		0.000171	0.0001668	0.000161	8.502E-05	5.82E-05				0.0001285	41.154
Acenaphthene		8.883E-05	8.85E-05	8.81E-05	8.699E-05	6.815E-05	5.69E-05			7.959E-05	17.2023
Phenanthrene			4.591E-05	4.58E-05	4.299E-05	3.825E-05	3.83E-05			4.226E-05	9.0195
Anthracene		0.000231	0.0002245	0.000234	0.0002565	0.0002352	0.000226			0.0002345	4.9344
Fluoranthene		0.0001888	0.0001813	0.000189	0.0002145	0.0001762	0.000154			0.000184	10.674
Pyrene		0.0001029	0.0001021	0.000104	0.0001091	0.0001218	9.98E-05			0.0001067	7.556
Chrysene			3.67E-05	3.8E-05	3.986E-05	3.314E-05	3.93E-05			3.74E-05	7.1468
Benz[a]anth			1.628E-05	1.32E-05	1.382E-05	1.29E-05	1.36E-05	1.56E-05	1.2E-05	1.398E-05	10.1041
Benzo[b]			2.057E-05	2.1E-05	2.461E-05	1.997E-05	2.07E-05	2.22E-05	1.5E-05	2.054E-05	14.5421
Benzo[k]					2.298E-06	2.12E-06	2.25E-06	2.32E-06	2.1E-06	2.21E-06	5.1776
Benzo[a]pyr			1.153E-05	9.37E-06	1.037E-05	9.282E-06	9.69E-06	9.84E-06	9.3E-06	9.914E-06	8.1593
Dibenz[a,h]			2.221E-05	2.27E-05	2.344E-05	2.266E-05	2.44E-05	1.93E-05	2.5E-05	2.288E-05	8.5263
Benzo[ghi]+Indeno			2.928E-05	2.87E-05	2.976E-05	1.932E-05	3.01E-05	3.35E-05	2.8E-05	2.844E-05	15.3133

UV Detector

Compounds	Conc(µg/L) RT	1000	500	200	100	50	20	RFP (ppb/area)	R^2
Naphthalene	7.224	27132	13920	4849	2777	1254	550	0.0368	0.9991
Acenaphthylene	8.03	19244	9465	4268		1964	611	0.0517	0.995
Fluorene	9.82	130232	66673	28450	13616	6520	3003	0.0076	0.9994
Acenaphthene	10.185	9434	4984	2201	1053	497		0.1041	0.9996
Phenanthrene	10.667	330956	173130	71897	33073	16507	6844	0.003	0.9991
Anthracene	11.369	807355	420243	173682	79468	39793	15703	0.0012	0.9993
Fluroanthene	13.181	80324	41924	18200	7837	3763	1561	0.0123	0.9986
Pyrene	14.261	67591	32595	14301	6702	3315	1101	0.0149	0.9994
Chrysene	17.462	286431	149289	61162	28612	13999	5351	0.0035	0.9995
Benzo(a)anthracene	17.994	199978	104229	45561	19764	9510	3905	0.0049	0.9987
Benzo (b)fluoranthene	23.16	220954	114898	47896	20987	11087	3414	0.0045	0.9992
Benzo (k) fluoranthene	24.073	157416	80987	33476	14333	8103	2521	0.0063	0.9994
Benzo (a) pyrene	25.261	202442	110268	44891	19536	10862	4605	0.0048	0.9974
Dibenz (a,h) anthracene	30.389	44450	21179	10156	4918	3759	1321	0.0225	0.9962
Benzo(ghi) + Indeno	32.769	257487	134822	54300	24542	9315	3877	0.0077	0.9991

Compounds	Conc(µg/L)	1000	500	200	100	50	20	mean RSF	RSD(%)
Naphthalene		0.0368568	0.0359195	0.0412456	0.0360101	0.0398724	0.0363636	0.0377114	6.0250255
Acenaphthylene		0.0519642	0.0528262	0.0468604		0.0254582	0.0327332	0.0419685	29.173113
Fluorene		0.0076786	0.0074993	0.0070299	0.0073443	0.0076687	0.00666	0.0073135	5.4776908
Acenaphthene		0.1059996	0.100321	0.0908678	0.0949668	0.1006036		0.0985518	5.8884257
Phenanthrene		0.0030215	0.002888	0.0027818	0.0030236	0.003029	0.0029223	0.0029444	3.3796416
Anthracene		0.0012386	0.0011898	0.0011515	0.0012584	0.0012565	0.0012736	0.0012281	3.8604683
Fluroanthene		0.0124496	0.0119263	0.010989	0.01276	0.0132873	0.0128123	0.0123707	6.5665336
Pyrene		0.0147949	0.0153398	0.013985	0.0149209	0.015083	0.0181653	0.0153815	9.3523416
Chrysene		0.0034912	0.0033492	0.00327	0.003495	0.0035717	0.0037376	0.0034858	4.7335582
Benzo(a)anthracene		0.0050006	0.0047971	0.0043897	0.0050597	0.0052576	0.0051216	0.0049377	6.2425694
Benzo (b)fluoranthene		0.0045258	0.0043517	0.0041757	0.0047649	0.0045098	0.0058582	0.0046977	12.801977
Benzo (k) fluoranthene		0.0063526	0.0061738	0.0059744	0.0069769	0.0061706	0.0079334	0.0065969	11.21822
Benzo (a) pyrene		0.0049397	0.0045344	0.0044552	0.0051188	0.0046032	0.0043431	0.0046657	6.4286693
Dibenz (a,h) anthracene		0.0224972	0.0236083	0.0196928	0.0203335	0.0133014	0.01514	0.0190955	21.342006
Benzo(ghi) + Indeno		0.0077674	0.0074172	0.0073665	0.0081493	0.0107354	0.0103173	0.0086255	17.445775

Note: RT means retention time

RSF means response factor
FLD means fluorescence detector
UV means Ultraviolet detector
RSD means relative standard deviation

Second source calibration verification

Standard from another source, Sigma Aldrich, was analyzed to check the accuracy of the initial calibration. This standard has all the PAHs in the initial calibration standard but with varied concentrations for each compound. The measured concentrations, which are chromatography peak area times its respective response factor, are compared to the expected concentrations. The relative differences as defined by difference between measured concentrations and expected concentrations divided by expected concentrations are listed in Table 2.

TablebB2 Second source standard check for accuracy of ICAL

compounds	Fluorescence detector Expected conc(ppb)	measured conc(PPb)	RD (%)	Expected conc(ppb)	measured conc(PPb)	RD (%)
Naphthalene	20	19.94	-0.32	50	47.91	-4.17
Acenaphthylene						
Fluorene	4	4.58	14.46	10	9.94	-0.63
Acenaphthene	20	19.10	-4.52	50	50.70	1.39
Phenanthrene	2	2.09	4.63	5	5.02	0.36
Anthracene	2	1.80	-10.13	5	4.59	-8.29
Fluroanthene	4	3.63	-9.24	10	10.04	0.38
Pyrene	2	1.81	-9.47	5	4.61	-7.71
Chrysene	2	1.76	-11.97	5	4.89	-2.18
Benzo(a)anthracene	2	2.00	0.16	5	5.06	1.24
Benzo (b)fluoranthene	4	4.07	1.79	10	10.04	0.38
Benzo (k) fluoranthene	2	2.15	7.67	5	5.22	4.37
Benzo (a) pyrene	2	1.89	-5.52	5	4.57	-8.52
Dibenz (a,h) anthracene	4	3.97	-0.68	10	9.62	-3.82
Benzo(ghi) + Indeno	2+4	3.99	-33.53	5+10	9.89	-34.10
	UV detector					
Naphthalene	1000	1033.64	3.36	500	495.66	-0.87
Acenaphthylene	2000	1993.60	-0.32	1000	921.50	-7.85
Fluorene	200	208.71	4.36	100	97.99	-2.01
Acenaphthene	1000	1163.84	16.38	500	478.13	-4.37
Phenanthrene	100	107.55	7.55	50	43.92	-12.16
Anthracene	100	97.79	-2.21	50	46.11	-7.78
Fluroanthene	200	189.20	-5.40	100	100.01	0.01
Pyrene	100	91.61	-8.39	50	59.64	19.29
Chrysene	100	92.38	-7.62	50	47.17	-5.65
Benzo(a)anthracene	100	85.20	-14.80	50	45.24	-9.53
Benzo (b)fluoranthene	200	209.18	4.59	100	96.26	-3.75
Benzo (k) fluoranthene	100	101.27	1.27	50	50.02	0.04
Benzo (a) pyrene	100	98.34	-1.66	50	40.46	-19.08
Dibenz (a,h) anthracene	200	200.23	0.11	100	109.15	9.15
Benzo(ghi) + Indeno	100+200	266.31	-11.23	50+100	116.33	-22.45

RD Means relative difference as defined previously.
The relative difference between the measured concentrations and expected concentrations are within 20% except benzo[ghi] perylene and indino[1,2,3-cd]pyrene. This is because these two compounds coelute from the column and are considered as one compound. The chromatography shows good separation for the peaks except for benzo[ghi] perylene and indino[1,2,3-cd]pyrene (the last peak)

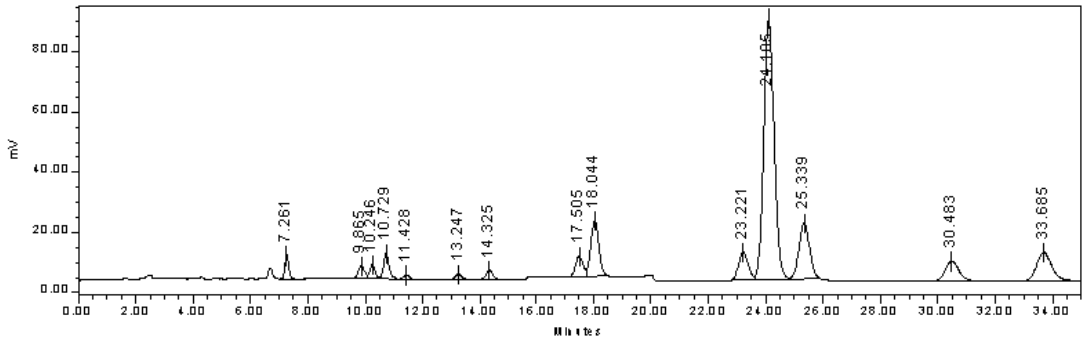


Figure 1 Chromatography of 5 ppb PAHs by Fluorescence detector (Acenaphthylene has no fluorescence signal)

Instrument Method detection limit (MDL)

Detection limits of PAHs by HPLC were determined by repeatedly measuring a standard whose concentration is one to five times of the practical detection limit, usually seven replicates were used. The method detection limit can then be estimated by mimimum concentration that can be determined to be nonzero with 99% confidence.

$$MDL=SD*t_{0.99}$$

Where MDL, method detection limit and SD, standard deviation of the measurements of the low concentration standard. $t_{0.99,}$ is the t-distribution table value corresponding to 99% confidence with the degree of freedom (n-1). Here t is 3.143.

Method detection limits are as shown in Table B3. Actual detection limits were lower than expected values for all compounds.

Table B3 Method detection limit (MDL) via direct injection

Compounds	Exp. MDL µg/L	Measured Conc							stdev	Actual MDL (µg/L)
Naphthalene	1	1.0133	1.0419	1.0273	0.9819	1.0409	0.9999	1.0374	0.0230	0.0722
DBF	1	0.9609	0.9379	0.9031	0.9664	0.8450	0.8883	0.8993	0.0433	0.1362
2-MNP	1	0.8481	0.8909	0.8671	0.7973	0.9882	0.8797	0.8246	0.0610	0.1917
Fluorene	1	1.8967	2.2384	2.0020	1.5652	1.8315	1.4680	1.8182	0.2589	0.8137
Acenaphthene	1	1.0182	1.0395	0.9541	0.8799	0.8860	0.7484	0.8517	0.1012	0.3180
Phenanthrene	1	1.0126	1.1176	1.1529	0.9491	1.1065	1.0413	1.1217	0.0729	0.2290
Anthracene	1	0.8143	0.8053	0.9789	0.8941	0.9354	0.7959	0.8449	0.0708	0.2224
Fluoranthene	1	0.8160	0.7639	0.8659	0.8189	0.8176	0.9749	0.8719	0.0669	0.2103
Pyrene	1	1.0214	0.8728	0.8857	0.8102	0.8442	0.9004	0.9066	0.0663	0.2085
Chrysene	0.2	0.1385	0.1230	0.1449	0.1312	0.1809	0.1370	0.1754	0.0222	0.0698
Benz[a]anthracene	0.2	0.1835	0.1635	0.1807	0.1745	0.1727	0.1728	0.1892	0.0085	0.0266
Benzo[b]fluoranthene	0.05	0.0569	0.0660	0.0378	0.0505	0.0705	0.0441	0.0577	0.0116	0.0365
Benzo[k]fluoranthene	0.05	0.0535	0.0510	0.0474	0.0512	0.0496	0.0485	0.0516	0.0021	0.0065
Benzo[a]pyrene	0.05	0.0505	0.0459	0.0405	0.0572	0.0499	0.0435	0.0422	0.0058	0.0183
Dibenz[a,h]anthracene	0.2	0.1315	0.1447	0.1428	0.1506	0.1388	0.1295	0.1291	0.0084	0.0263
Benzo[ghi]+Indeno	0.2	0.1801	0.1570	0.1804	0.1469	0.1519	0.1488	0.1523	0.0144	0.0454

Appendix C – Quality Assurance Checks

Laboratory control samples check

In this calibration study, samples are analyzed via direct injection, sorption onto SPME followed by extraction into solvent and direct injection, and liquid-liquid extraction. Only Liquid-liquid extraction provides significant potential for loss due to vaporization or sorption during processing. Liquid- liquid extraction may also lead to increases in reported concentration due to the effect of association of hydrophobic organics with dissolved organic matter. The latter effect is likely to be small, however, due to the very low levels of dissolved organic matter (dissolved organic carbon of 1.9 mg/L).

1 L site water (sea water from pacific sound bay in Seattle) was spiked with PAHs and mixed for three hours. 300 ml water was sequentially extracted with 30 ml+20ml +10 ml DCM. The extract was dried by passing through a sodium sulfate column and concentrated under gentle nitrogen flow to approximately 1 ml. 100 µl of the 1 ml extract was analyzed and the rest of the extract was diluted ten times since some compounds like Benz[a]anthracene, Benzo (b)fluoranthene, Benzo (k)fluoranthene and B[a]P saturated fluorescence detector but were not detectable on UV. For comparison, water samples were directly injected before liquid-liquid extraction. The concentrations by liquid-liquid extraction are compared to direct injection concentrations in the table below. Most compounds show good recovery except Naphthalene, which shows around 50% loss during extraction, however, in the acceptable range as defined by DOD

Table C1 Comparison between direction injection and liquid-liquid extraction

Compounds	Ratio of measured concentration LLE/direct injection (standard deviation)
Naphthalene	0.56 (0.065)
DBF	0.76 (0.079)
2-MNP	0.72 (0.086)
Fluorene	0.87 (0.078)
Acenaphthene	0.92 (0.093)
Phenanthrene	0.89 (0.067)
Anthracene	1.18 (0.13)
Fluoranthene	1.04 (0.053)
Pyrene	0.74 (0.035)
Chrysene	1.156 (0.41)
Benz[a]anthracene	0.971 (0.097)
Benzo (b)fluoranthene	1.02 (0.14)
Benzo (k) fluoranthene	0.95 (0.028)
Benzo (a) pyrene	0.90 (0.074)
Average	0.90 (0.10)

Continuous calibration verification

5 µg/L and 50 µg/L calibration standards with all 16 PAHs and 100µg/L DBF and 100 µg/L 2-MNP standard are analyzed at the beginning of each batch test to check Instrument response is reliable, and has not changed significantly from the current initial calibration curve. 5 µg/L standard of PAHs are then continuously analyzed every ten samples or after one group of data (no more than 12 samples). The following table lists a summary of the results. The difference between measured standard concentrations and the expected value (5ppb or 50ppb) are within 10% except 5ppb Fluorene on FLD and 50ppb Acenaphthene on UV detector.

Table C2 continuous calibration verification

		5 ppb standard			Fluorescence detector				
		24-Nov		1-Dec		11-Dec		15-Dec	
	compounds	Measured Conc	Diff(%)	Measured Co	Diff(%)	Measured Co	Diff(%)	Measured Co	Diff(%)
1	Naphthalene	4.94	-1.24	5.08	1.56	5.00	0.00	4.74	-5.22
2	Fluorene	7.49	49.85	6.33	26.51	6.48	29.68	5.03	0.54
3	Acenaphthene	5.19	3.70	5.50	10.05	5.27	5.33	4.58	-8.41
4	Phenanthrene	5.01	0.21	4.90	-1.96	5.07	1.34	4.60	-8.01
5	Anthracene	4.22	-15.69	4.91	-1.84	4.48	-10.37	3.95	-21.05
6	Fluoranthene	4.61	-7.80	5.24	4.76	4.78	-4.47	4.87	-2.62
7	Pyrene	4.65	-7.06	5.34	6.84	5.24	4.73	4.88	-2.50
8	Chrysene	4.60	-8.01	5.03	0.62	4.77	-4.60	4.83	-3.43
9	Benz[a]anth	4.96	-0.87	5.24	4.88	4.77	-4.54	4.80	-3.94
10	Benzo[b]	4.72	-5.64	5.27	5.47	4.87	-2.51	4.82	-3.67
11	Benzo[k]	5.16	3.25	5.47	9.48	5.16	3.22	5.08	1.65
12	Benzo[a]pyr	4.79	-4.21	4.49	-10.10	4.82	-3.62	4.57	-8.66
13	Dibenz[a,h]	4.50	-9.97	5.34	6.87	5.02	0.38	5.14	2.83
14	Benzo[ghi]+Inden	9.54	-4.62	10.58	5.79	10.42	4.24	9.84	-1.59
			50 ppb standard		UV detector				
1	Naphthalene	50.56	1.13	57.04	14.08	51.41	2.82	43.68	-12.64
2	Fluorene	50.82	1.64	53.02	6.04	44.86	-10.29	51.45	2.90
3	Acenaphthene	36.23	-27.55	60.48	20.96	42.47	-15.05	59.44	18.88
4	Phenanthrene	48.76	-2.48	52.25	4.49	48.86	-2.28	49.90	-0.20
5	Anthracene	48.25	-3.50	55.14	10.29	47.23	-5.54	48.12	-3.75
6	Fluoranthene	60.98	21.97	53.23	6.47	51.46	2.93	52.31	4.62
7	Pyrene	58.45	16.91	54.22	8.44	48.75	-2.49	43.82	-12.36
8	Chrysene	46.76	-6.48	53.42	6.83	51.10	2.19	52.40	4.80
9	Benz[a]anth	51.45	2.90	58.30	16.59	52.50	5.01	51.66	3.32
10	Benzo[b]	49.34	-1.32	53.40	6.79	52.38	4.76	53.79	7.59
11	Benzo[k]	44.82	-10.36	48.65	-2.69	49.67	-0.66	52.97	5.94
12	Benzo[a]pyr	49.48	-1.04	54.16	8.32	49.80	-0.40	45.70	-8.60
13	Dibenz[a,h]	53.33	6.65	58.41	16.82	71.60	43.19	56.30	12.59
14	Benzo[ghi]+Inden	96.61	-3.39	105.87	5.87	97.64	-2.36	96.10	-3.90

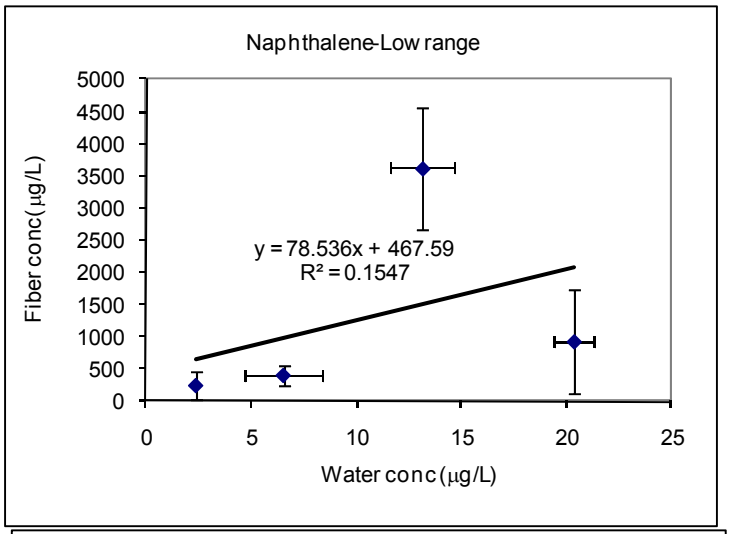
Appendix D

Figures of individual correlations of PDMS concentrations of PAHs to their corresponding water concentration. For each compound, the figures include

a) low range concentration calibration,
b) high range concentration calibration, and,
c) combined calibration.

In general, the low range calibration will provide the most accurate calibration in the low concentration range of interest

Naphthalene



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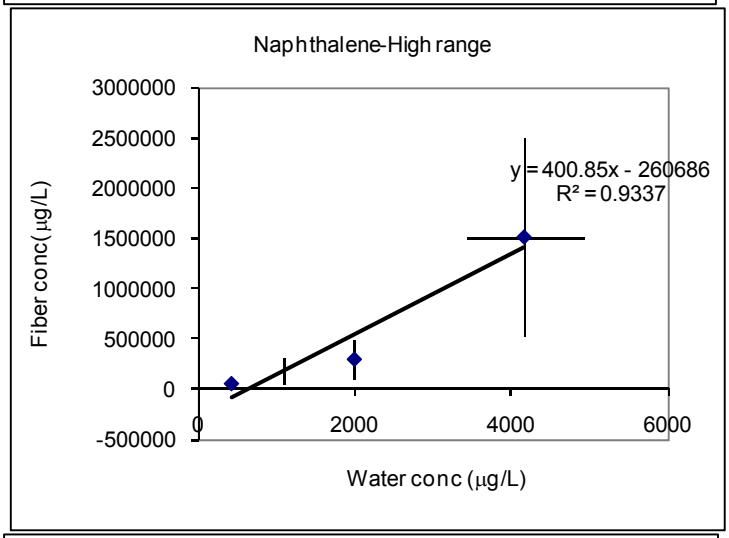

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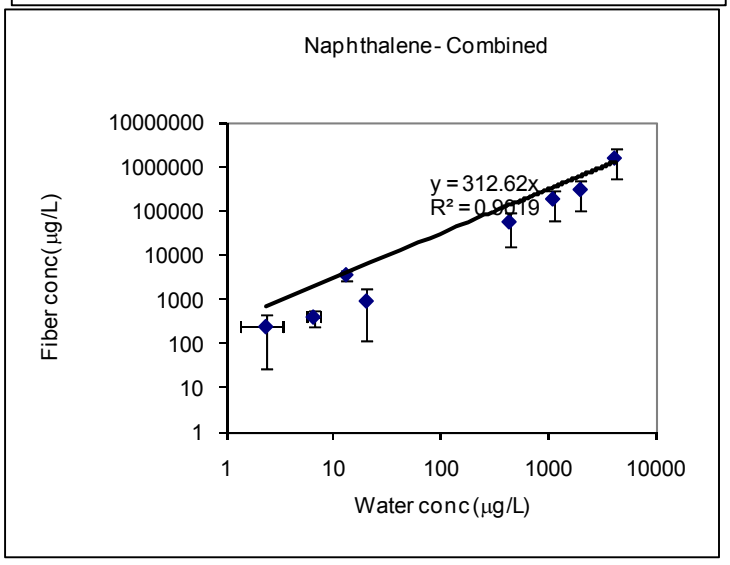
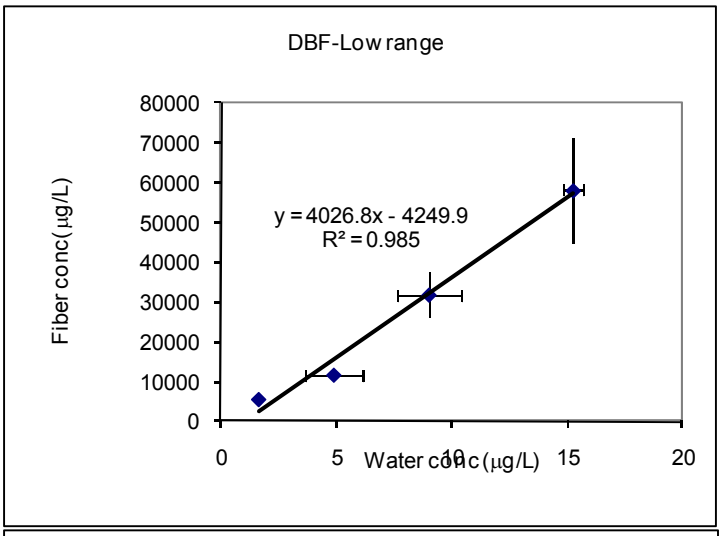


c)

Dibenzofuran- DBF

a)



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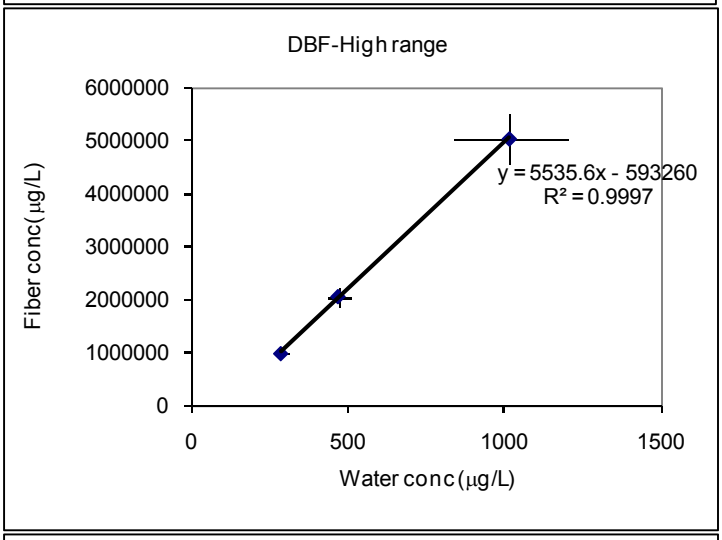

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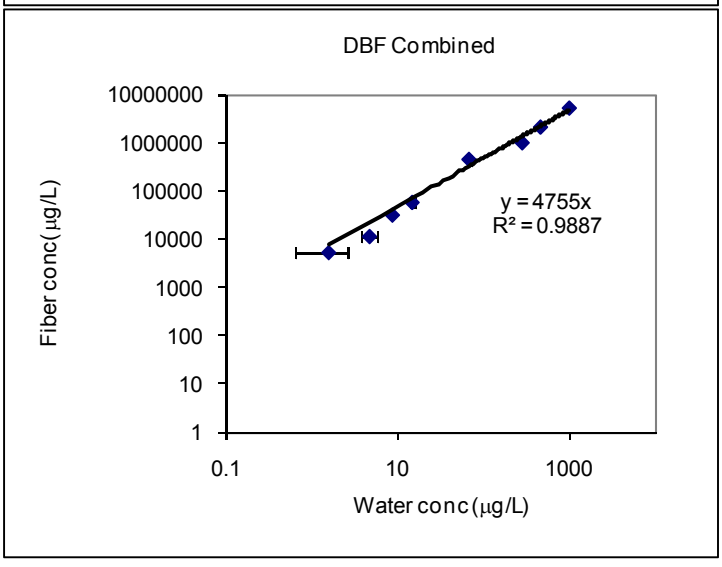
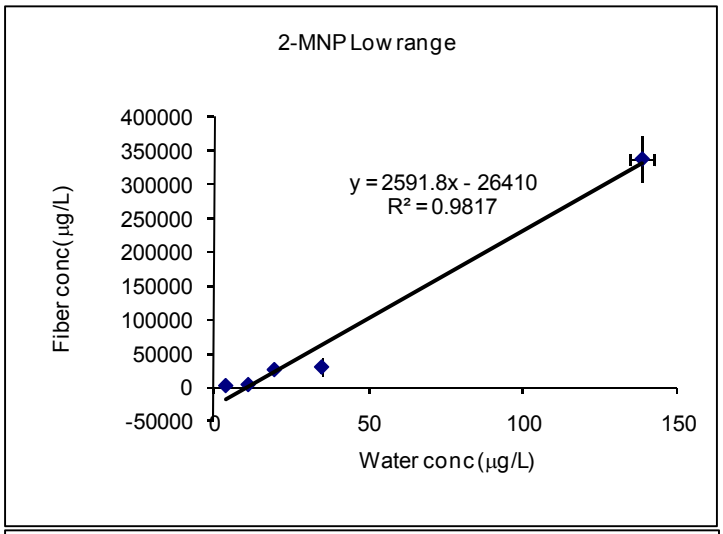


2 – Methylnaphthalene

a)



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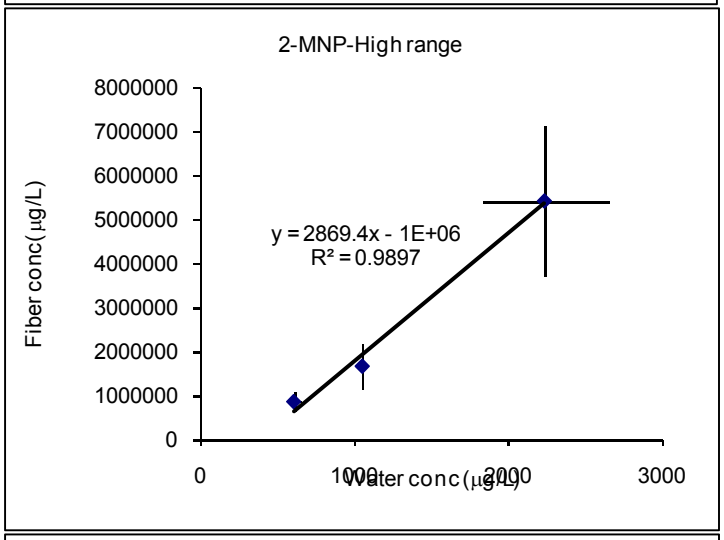

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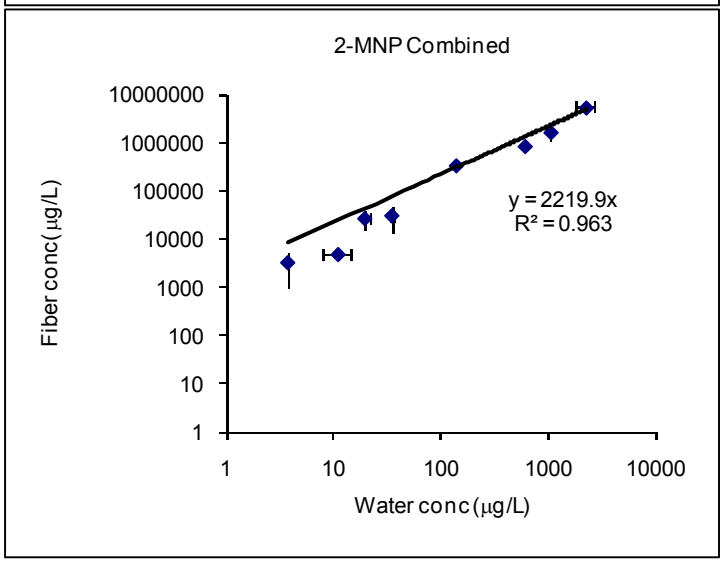
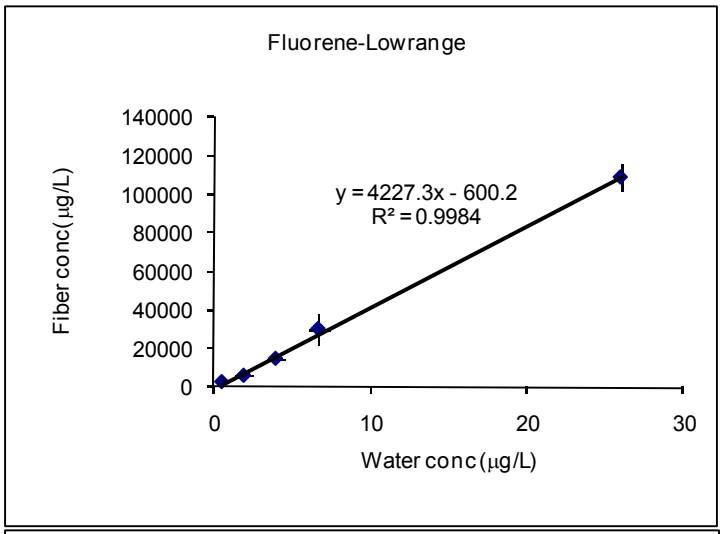


Fluorene

a)



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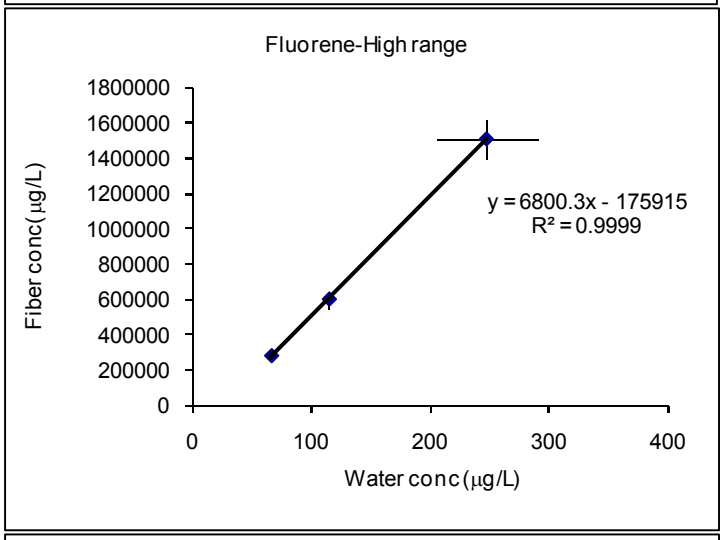

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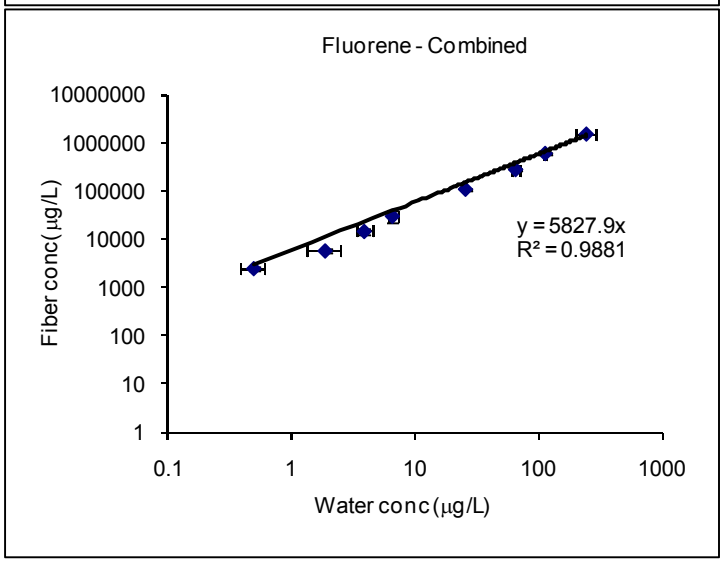
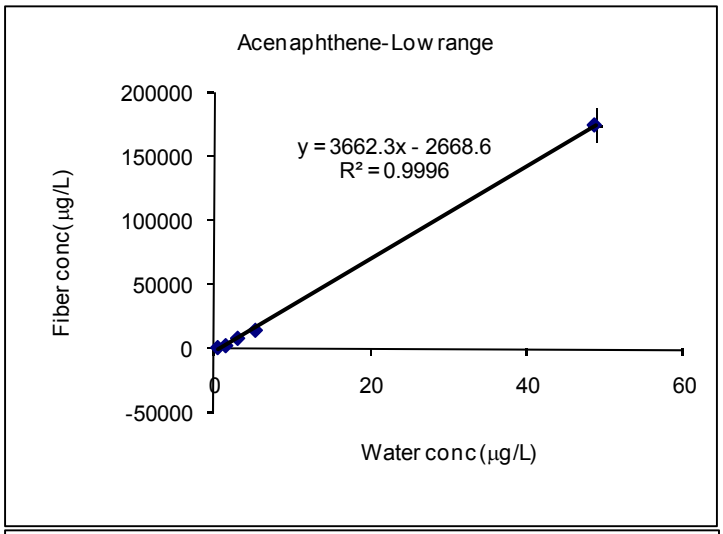


Acenapthene

a)



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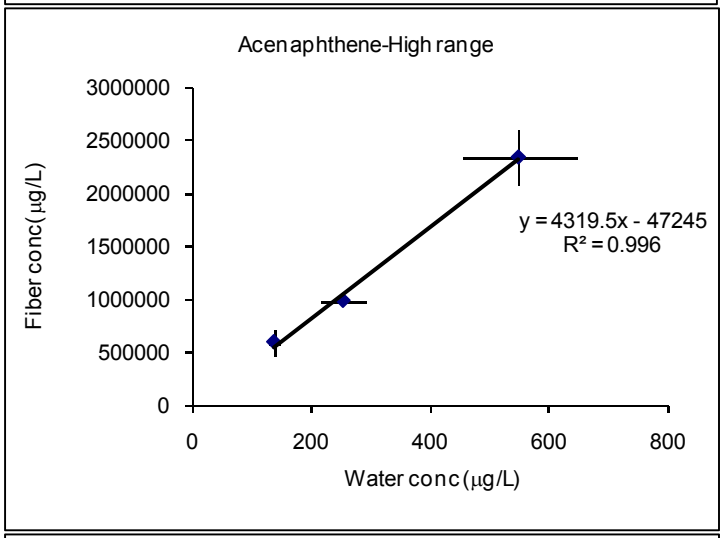

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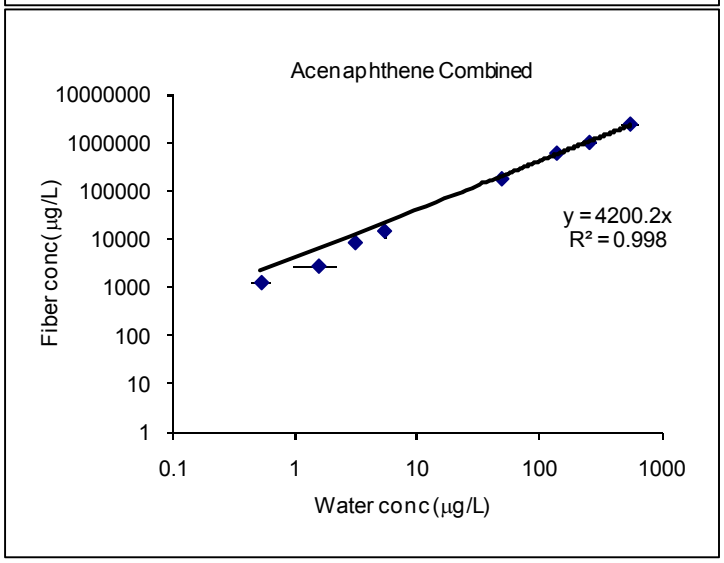
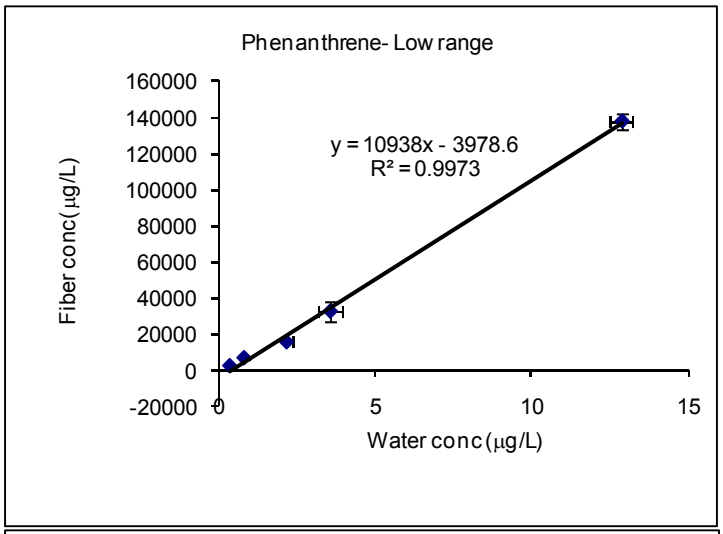


Phenanthrene

a)



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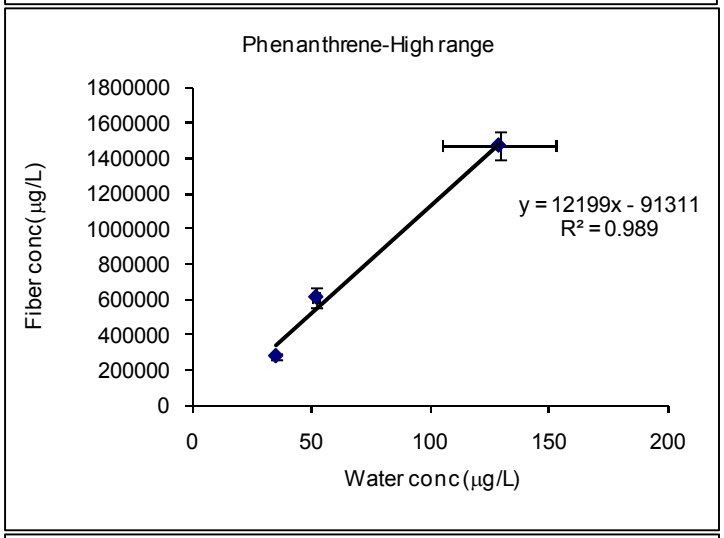

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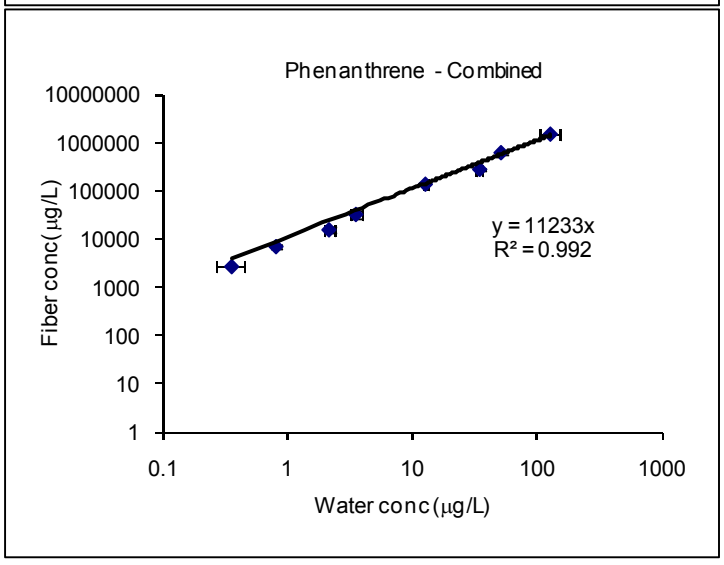
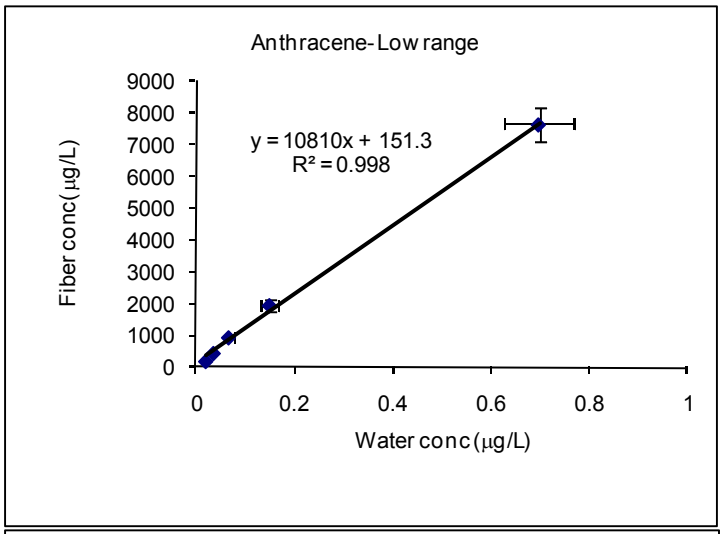


Anthracene

a)



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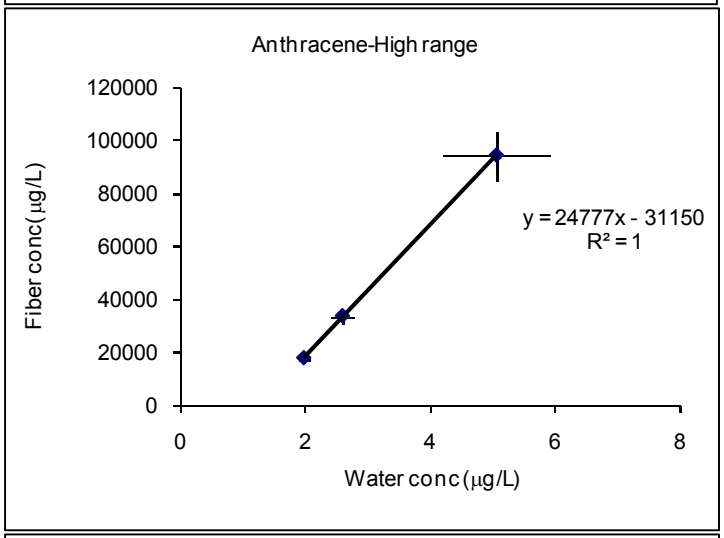

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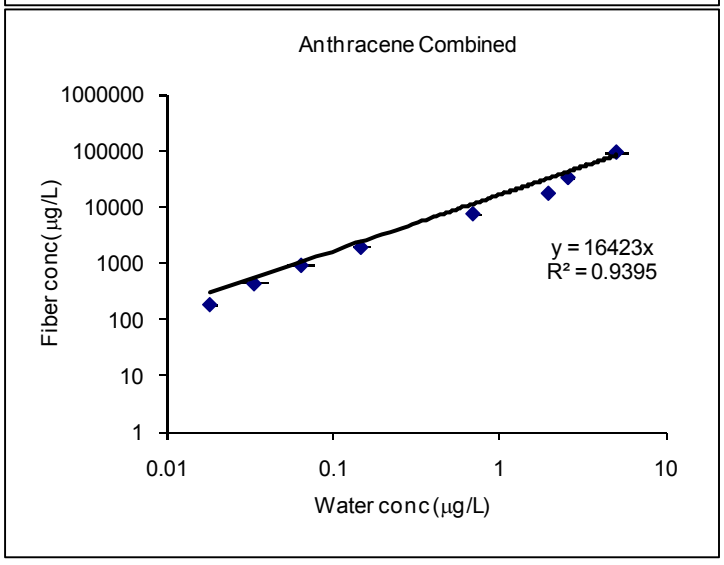

Fluoranthene

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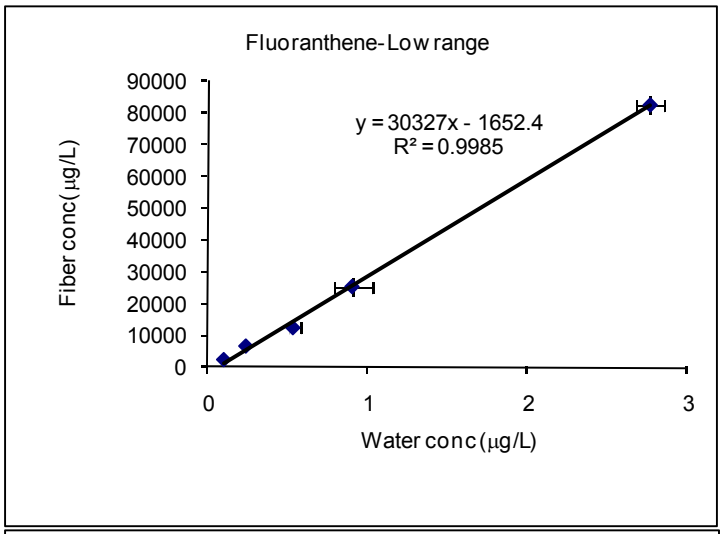

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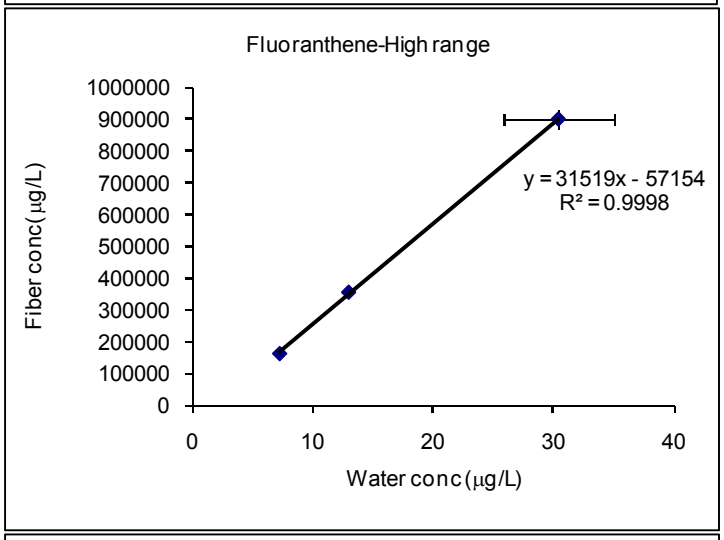

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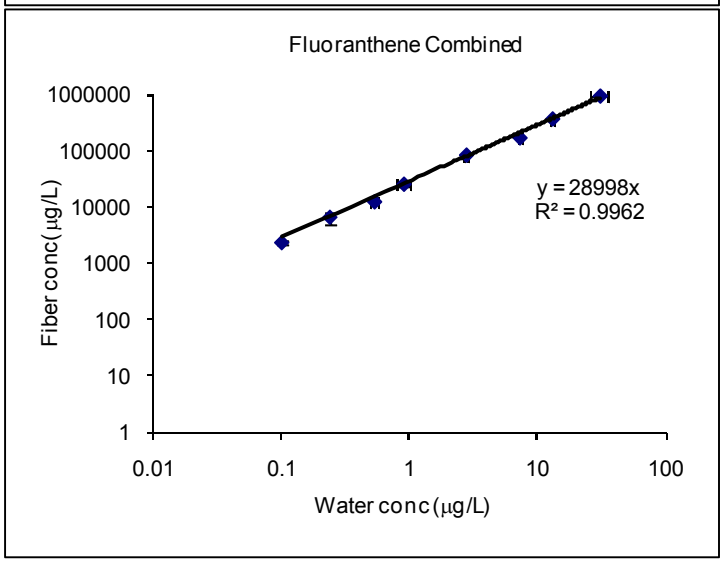
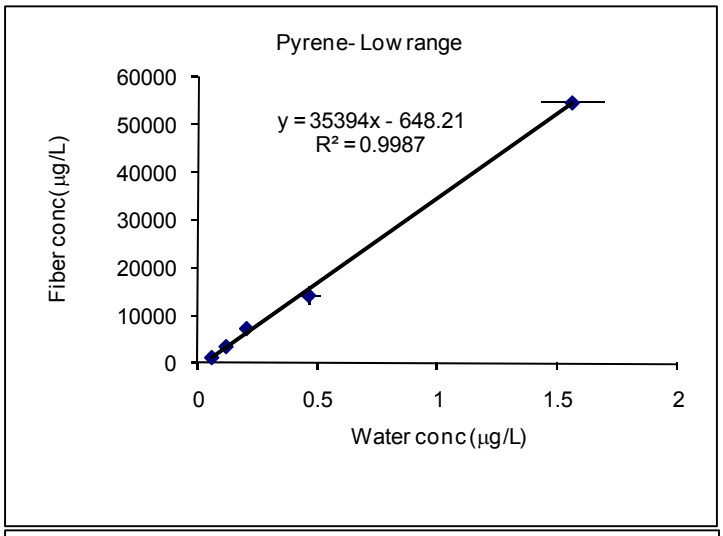


Pyrene

a)


Pyrene- Low range
y = 35394x - 648.21
R² = 0.9987
Fiber conc (µg/L)
Water conc (µg/L)
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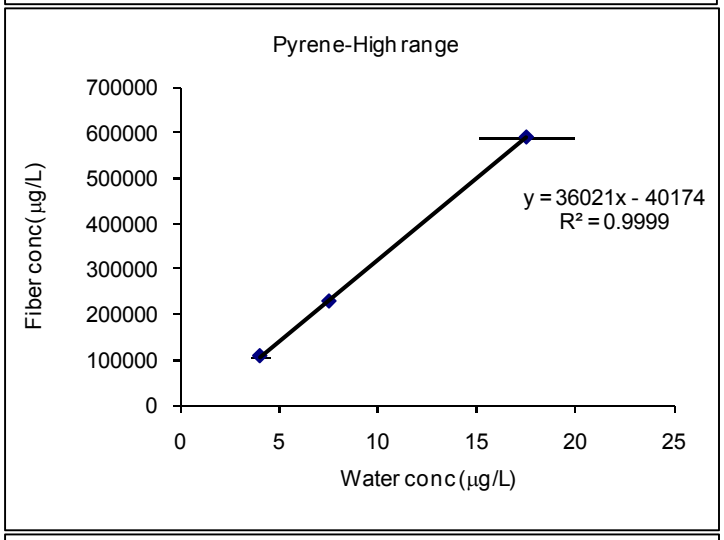
50000
40000
30000
20000
10000
0
0
0.5
1
1.5
2

b)


Pyrene-High range
y = 36021x - 40174
R² = 0.9999
Fiber conc (µg/L)
Water conc (µg/L)
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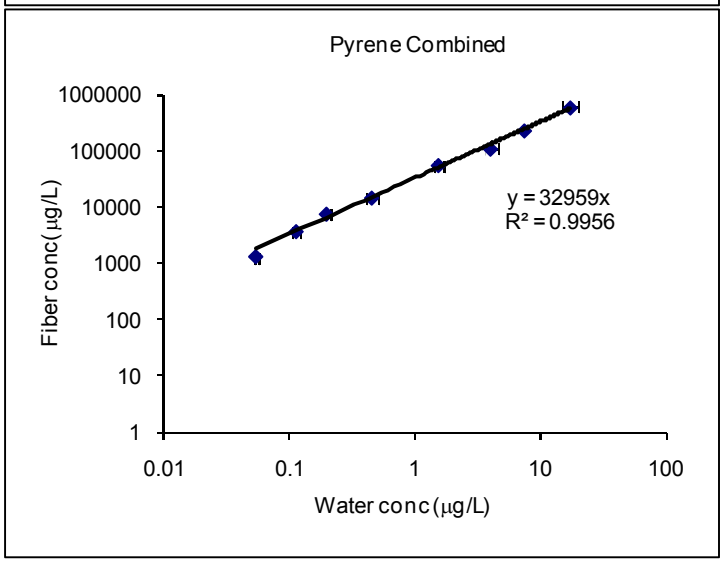
600000
500000
400000
300000
200000
100000
0
0
5
10
15
20
25

c)


Pyrene Combined
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R² = 0.9956
Fiber conc (µg/L)
Water conc (µg/L)
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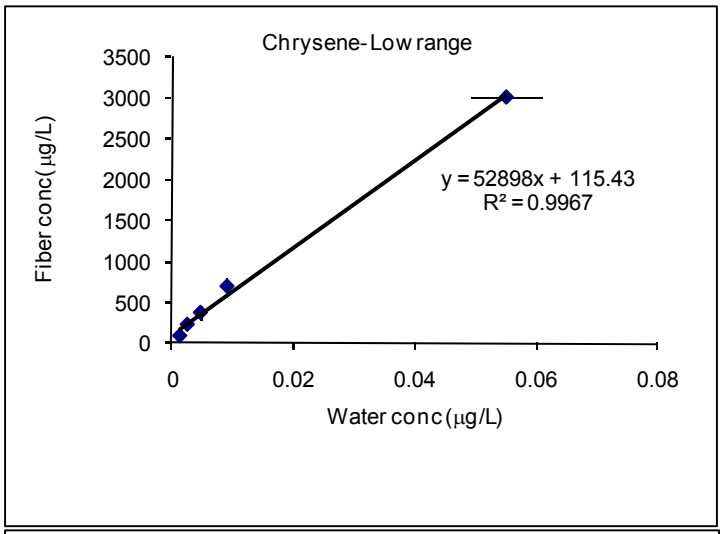
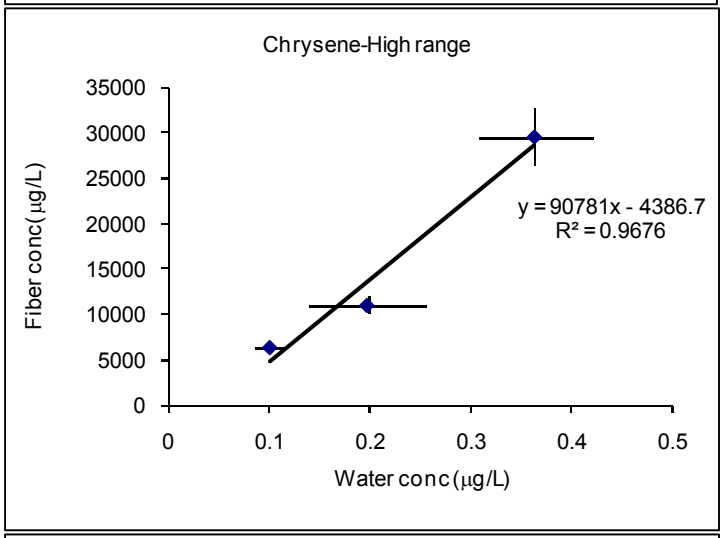
100000
10000
1000
100
10
1
0.01
0.1
1
10
100

Chrysene

a)



b)



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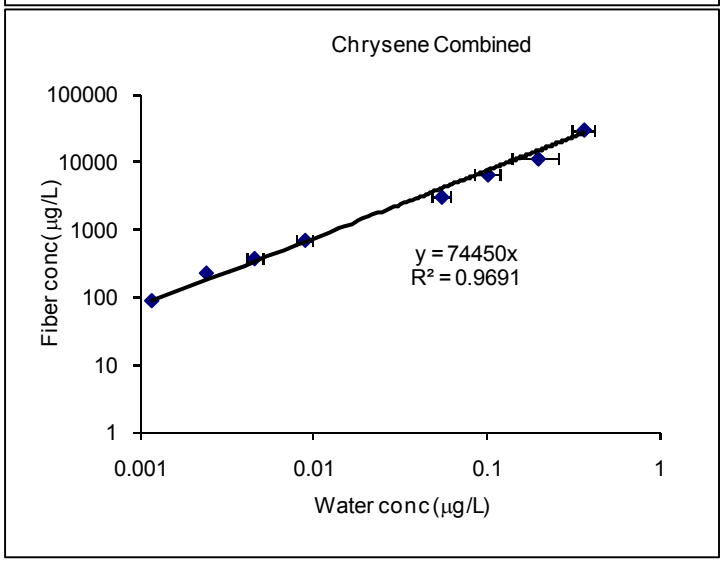
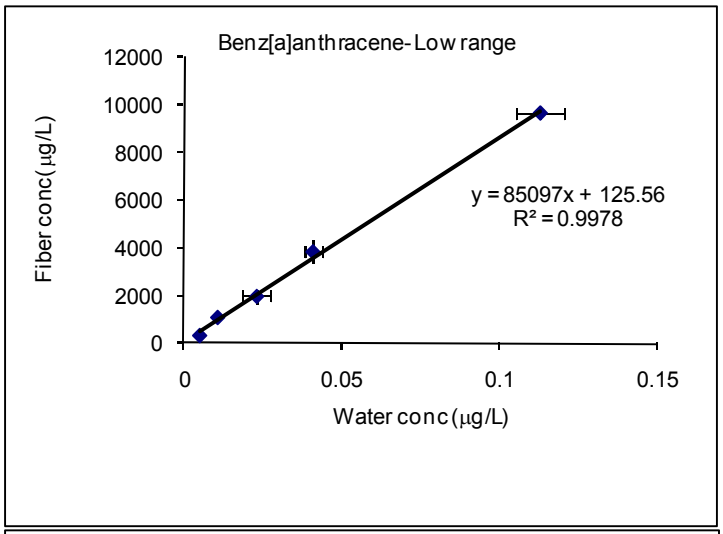


Benzo[a]anthracene

a)



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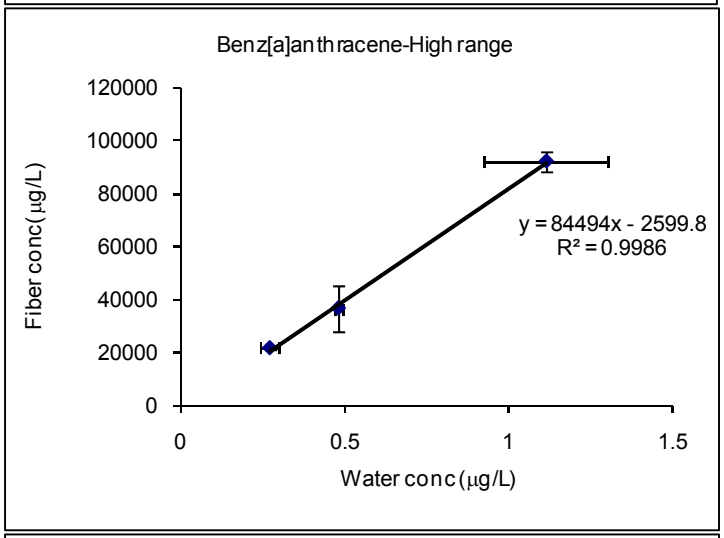

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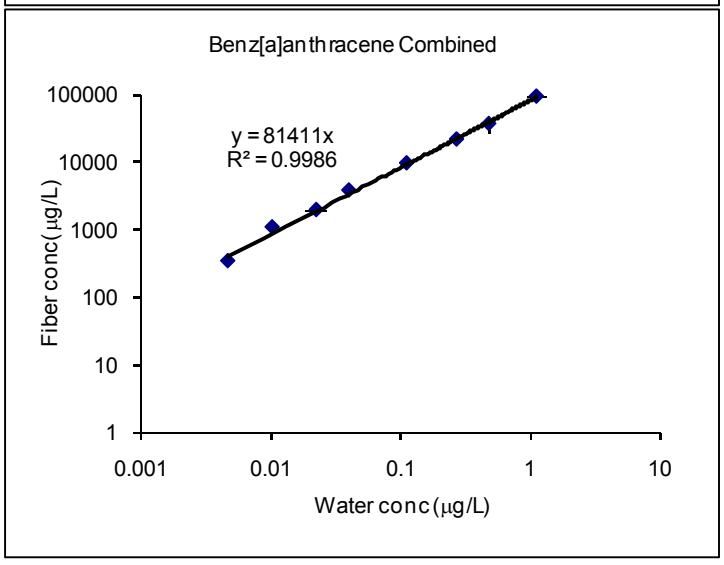
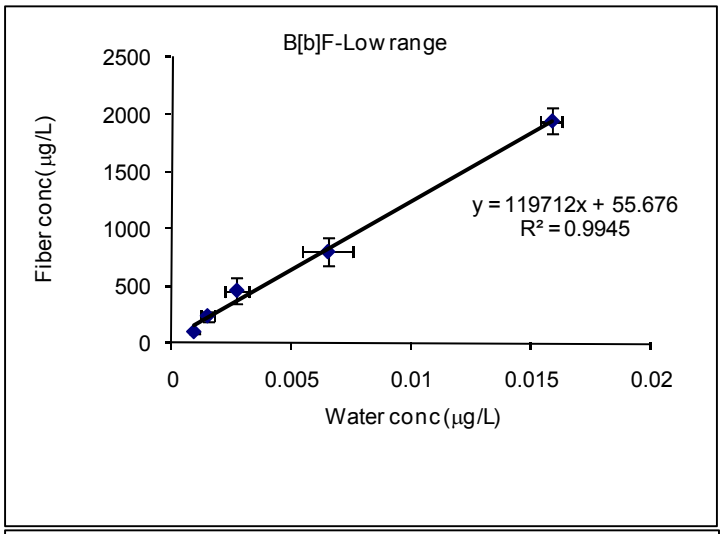


Benzo[b]fluoranthene BbF

a)



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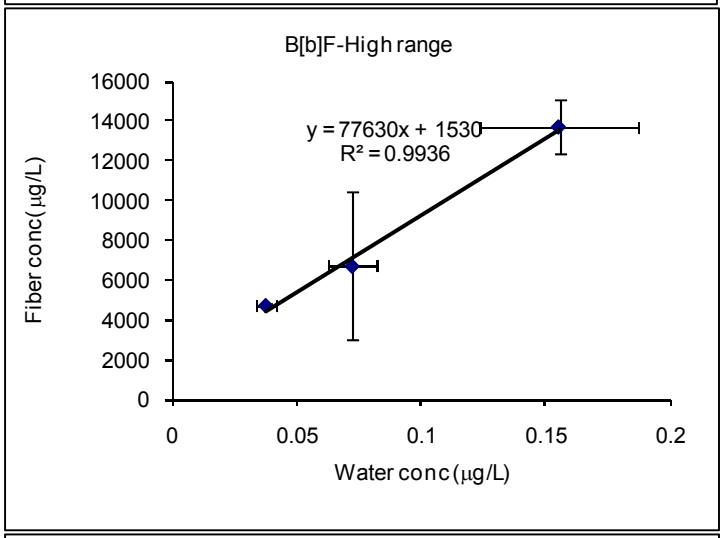

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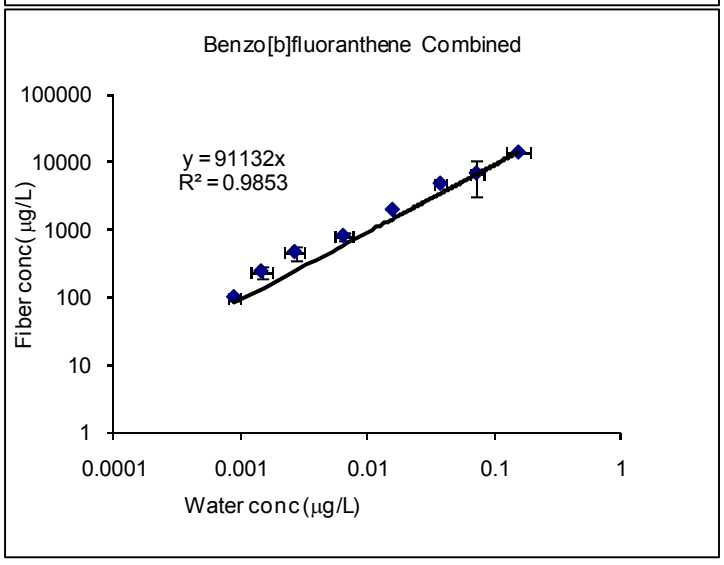
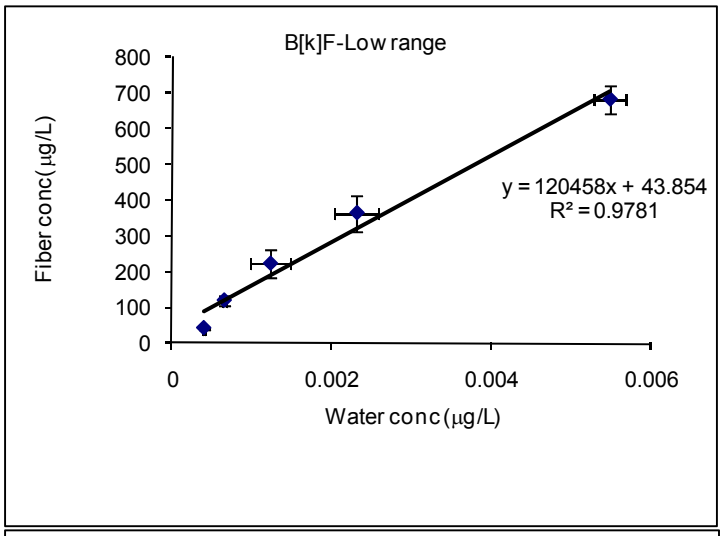


Benzo[k]fluoranthene BkF

a)



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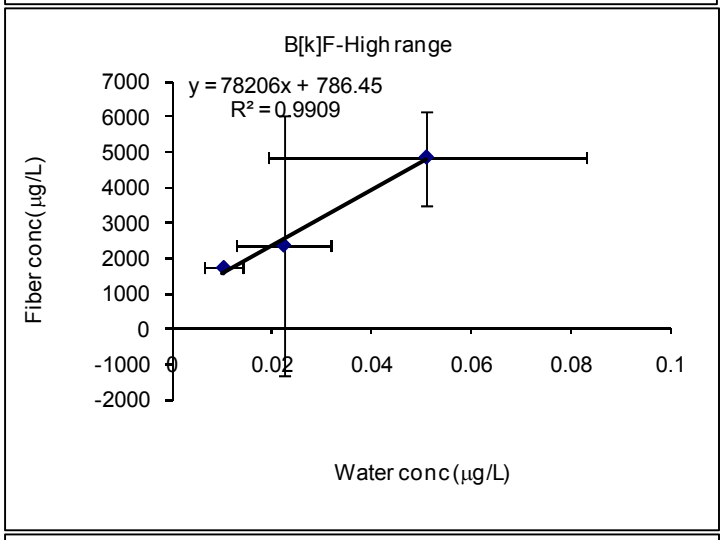
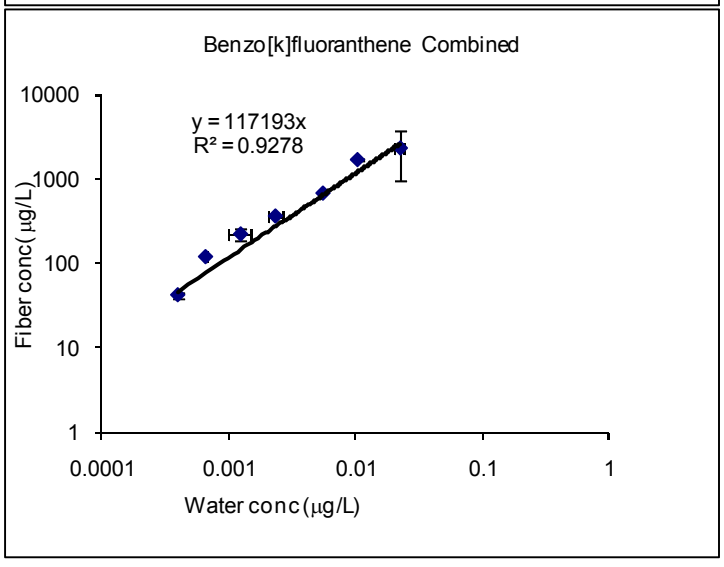
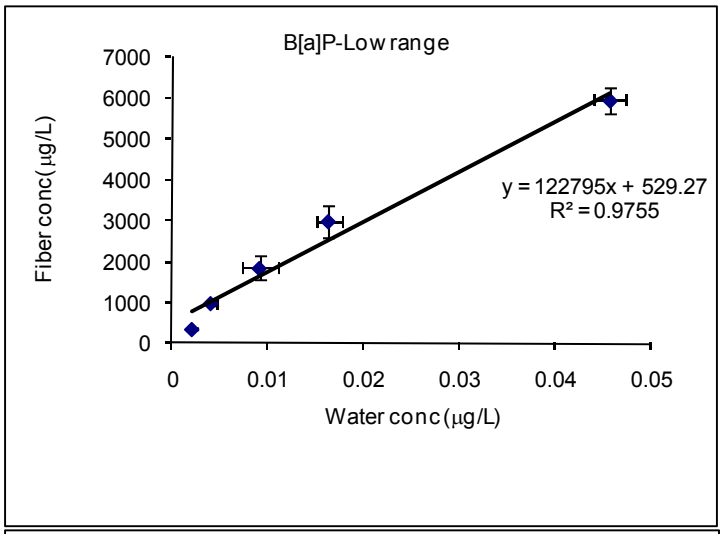


c)



Benzo[a]pyrene BaP

a)



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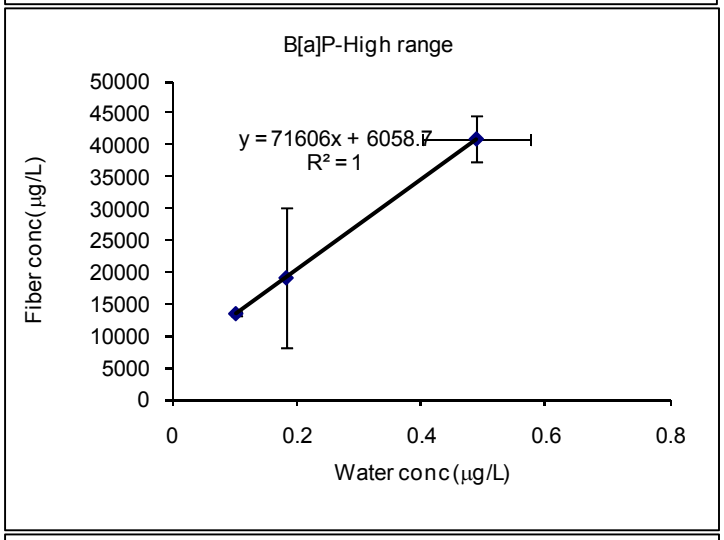
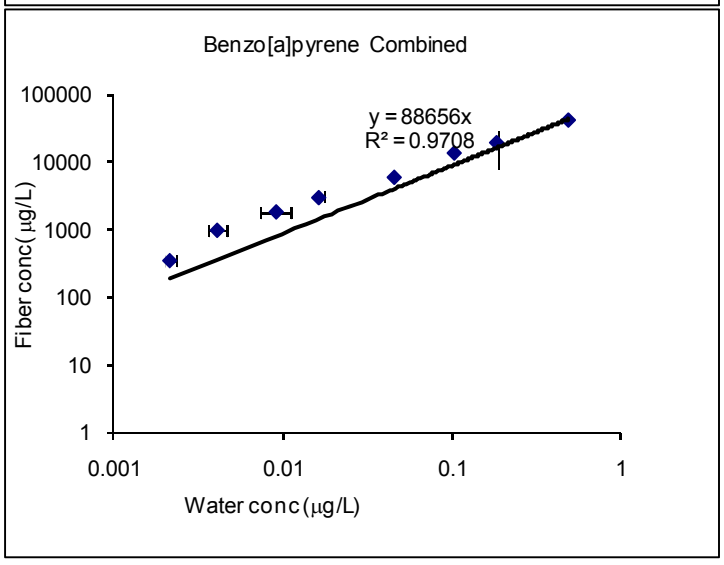
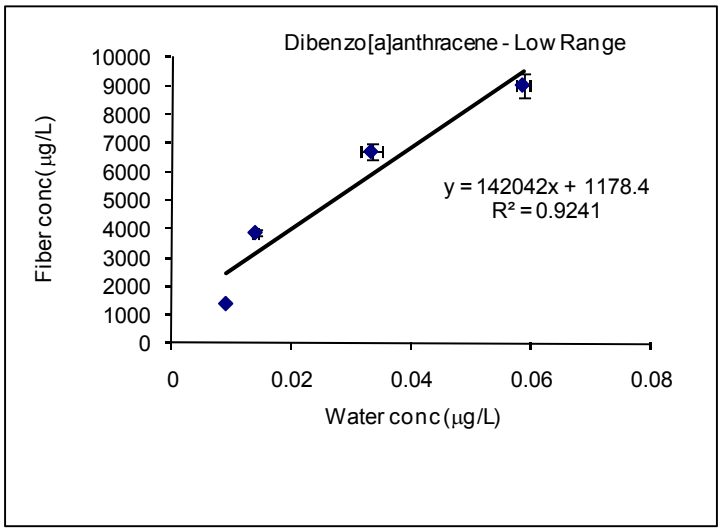


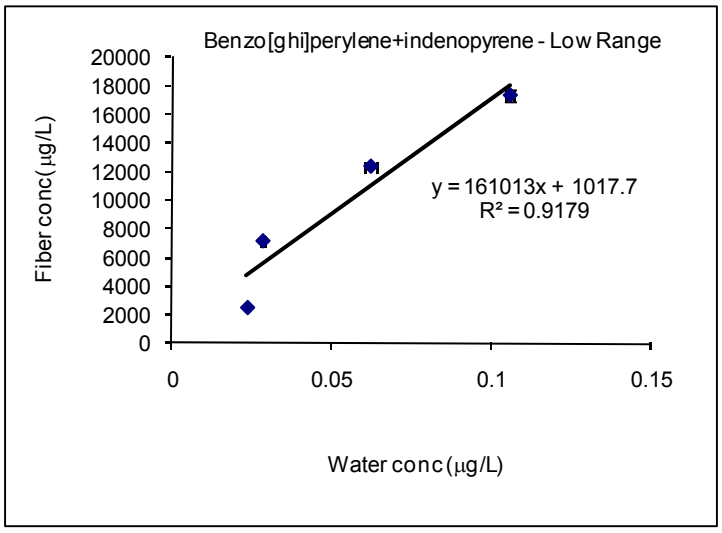
c)



Dibenzo[a]anthracene (low range only)



Benzo[g,h,i]perylene and indenopyrene (low range only)



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APPENDIX B

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Method Detection Limits and Practical Quantitation Limits (ug/L)

$$C_{\det\, water\, by\, SPME} = \frac{C_{\det SPME}}{K_{f-w}} = \frac{n_{detection}}{V_{PDMS} * K_{f-w}} = \frac{C_{\det, water\, by\, DI} * V_{solvent}}{V_{PDMS} * K_{f-w}}$$

$C_{det,\ water\ by\ SPME}$ is the detection limit of water by SPME

$C_{det,SPME}$ is the detection limit of fiber concentration

K_{f-w} is fiber-water partition coefficient

$n_{detection}$ is the mass of contaminant detected

V_{PDMS} is the volume of PDMS coating — V_{PDMS}=PDMS coating concentration (uL/m) * length of fiber (cm)

$V_{solevnt}$ is the volume of solvent used to extract SPME, like 100 uL

$C_{det,\ water\ by\ DI}$ is the dection limit of water by direct injection, which is the measured MDL. If measured PQL is used, then the equation will give the PQL of water by SPME

Compound	MDL by direct injection	PQL by direct injection	Kow	predicted *K*f	MDL by SPME		PQL by SPME	
	(water/SPME extract concentrations)				(SPME water exposure concentrations)			
	ug/L	ug/L			ug/L	ng/L	ug/L	ng/L
Naphthalene	0.072	0.50	3.37	2.41	0.29093	290.93	2.80086	2800.86
Dibenzofuran	0.136	1.00	4.30	3.40	0.05670	56.70	0.57879	578.79
2-Methylnaphthalene	0.192	1.00	3.90	2.97	0.21183	211.83	1.53646	1536.46
Fluorene	0.814	1.00	4.18	3.27	0.45387	453.87	0.77575	775.75
Acenaphthene	0.318	0.50	3.92	3.00	0.33455	334.55	0.73163	731.63
Phenanthrene	0.229	0.50	4.57	3.68	0.04931	49.31	0.14972	149.72
Anthracene	0.222	1.00	4.54	3.65	0.05153	51.53	0.32220	322.20
Fluoranthene	0.210	1.00	5.22	4.37	0.00927	9.27	0.06128	61.28
Pyrene	0.209	0.50	5.18	4.33	0.01013	10.13	0.03378	33.78
Chrysene	0.070	0.10	5.86	5.05	0.00064	0.64	0.00129	1.29
Benzo(a)anthracene	0.027	0.05	5.91	5.10	0.00022	0.22	0.00057	0.57
Benzo(b)fluoranthene	0.036	0.05	5.80	4.99	0.00039	0.39	0.00074	0.74
Benzo(k)fluoranthene	0.006	0.05	6.00	5.20	0.00004	0.04	0.00046	0.46
Benzo(a)pyrene	0.018	0.05	6.04	5.24	0.00011	0.11	0.00041	0.41
Dibenz(a,h)anthracene	0.026	0.10	6.75	6.00	0.00003	0.03	0.00015	0.15
Benzo(g,h,i)perylene & Ideno(1,2,3-cd)pyrene [1]	0.045	0.10	6.50	5.73	0.00009	0.09	0.00027	0.27

Notes

1. Benzo(g,h,i)perylene and ideno(1,2,3-cd)pyrene co-elute and may not be analytically separated by the laboratory, although efforts are underway to separate them.

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APPENDIX C

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STANDARD OPERATING PROCEDURE: Total and Dissolved Organic Carbon Analysis

1.0 Purpose/Applicability

This SOP is based upon Standard Method 5310b and is applicable in determining the amount of dissolved organic carbon in PSR-derived seawater.

2.0 Summary of Method

A measured volume of sample, here is 40 mL, is analyzed for dissolved organic carbon using Tekmar Dohrmann Apollo 9000.

3.0 Interferences

Unwanted organic chemicals can be introduced into the sample extract through contaminated reagents, glassware, chemicals or through poor technique. Sample blanks are analyzed to insure that contaminants are not introduced into the sample extract.

4.0 Apparatus

The Tekmar Dohrmann Apollo 9000 consists of an IC sparger, furnace, moisture control system, corrosives scrubber and the non dispersive infrared detection system (NDIR).

5.0 Operating Conditions

The Tekmar Dohrmann Apollo 9000 operates at 670ºC. The injection volume of the sample is 0.5mL and the sparge volume is 0.5 mL. The TOC method used in the quantification of DOC, first acidifies the sample in the IC sparger unit (removing inorganic carbon) and then combusts the sample to carbon dioxide. The carbon dioxide is then swept away with a carrier gas into the NDIR system.

6.0 Reagents

Carbon Stock Standard (SS) (1000mg/L)
Primary dilution standard (PDS) (100mg/L)
Phosphoric Acid (reagent grade and 20%)

7.0 Standards Preparation and Standard Curve

7.1 SS- 1000 mg/L carbon stock standard is prepared by dissolving 212.54mg of dried (at 103ºC for 2 hours) and cooled potassium hydrogen pythalate into a total volume of 100 mL DI water. 100uL of reagent grade phosphoric acid is added to prevent bacterial degradation of the standard. This standard can be stored for up to 1 month in 4ºC.

7.2 PDS- 10mL of the above 1000mg/L SS is diluted with DI to 100mL. This 100 mg/L PDS will be diluted further to get the following concentrations: 1, 2, 4, 5, and 10mg/L standards. Two drops of reagent grade phosphoric acid is added to these standards which can be stored for up to one month.

7.3 DOC Standards of 1, 2, 4, 5, and 10mg/L are analyzed on the Tekmar Dohrmann Apollo 9000. A response factor (RSF) is determined, with units of concentration/response, by plotting the DOC concentration versus the Apollo 9000's NDIR measurements. The slope of the linear curve with an intercept of zero is this RSF.

8.0 Sample Procedure

8.1 After equilibrium is established for the PSR-derived seawater calibration sample (spiked with 16PAH, DBF and 2-MNP), 40mL is transferred to a new 40mL vial.

8.2 Two drops of reagent grade phosphoric acid is added to the sample. The sample is capped with a Teflon-lined screw cap and can be stored at 4ºC for no longer than three weeks prior to analysis.

8.3 Turn on the Apollo 9000 and open the Oxygen supply. Ensure 20% Phosphoric acid and DI water are available for the run.

8.4 Load samples to the sample rack.

8.5 Set up the sample run with selecting the appropriate method.

8.6 Initiate run and verify the needle is automatically rinsed with DI water to prevent cross sample contamination.

8.7 After the run is complete, shut down the system and record data.

9.0 Calculation

9.1 Using the standard curve established in part 7.0, the DOC content in the PSR-derived seawater calibration sample can be calculated. The NDIR measurements for the samples multipled by RSF gives the DOC concentration in the samples.

10.0 Quality Control

10.1 All quality control data should be maintained and available for easy reference or inspection.

10.2 At least two Milli-Q water sample blanks will be analyzed for the five point calibration curve to determine background DOC concentration.

10.3 PSR-derived seawater sample blanks (not spiked) will be analyzed to compare the background DOC concentration.

Reference APHA, AWWA and WEF. 1992. Method 5310 Total Organic Carbon (TOC). *Standard Methods for the Examination of Water and Wastewater 18Ed.*

STANDARD OPERATING PROCEDURE: PAH analysis by High Performance Liquid Chromatography (HPLC)

1.0 Purpose/Applicability

This SOP is based on EPA standard method 8310 in SW846 series. This method is developed for polycyclic aromatic hydrocarbons (PAHs), but is applicable to Dibenzofuran (DBF). This method works for all matrices, water, fiber and sediment.

2.0 Interferences

Unwanted organic chemicals can be introduced into the samples through contaminated reagents, glassware, chemicals or through poor technique. Reagent and sample blanks are analyzed to insure that contaminants are not introduced into the samples.

3.0 Apparatus

The HPLC model is Waters 2795 (Waters, Milford, MA, USA) with ultraviolet-diode array (PAD 996) and fluorescence detectors (FLD 2475). The column is Phenomenex (Torrance, CA, USA) Luna 5µ C18 column (250*4.6 mm).

4.0 Operating conditions

4.1 HPLC is operated at isocratic condition. The mobile phase is acetonitrile (ACN) and water. The flow rate is 1.0 ml/min, and the ACN to water ratio is 70 % ACN and 30% water. The temperature is set at 40 □C

4.2 Emission and excitation wavelengths used for different PAHs in fluorescence detector are optimized to give good sensitivity as shown in the following table

Table 1 Emission and excitation wavelengths for selected PAHs

	Naph-thalene	Dibenzofuran 2-Methylnaphthalene Fluorene Acenaphthalene phenanthrene	Anthra-cene	Fluoranthene pyrene	Chrysene B[a]A	B[b]F B[k]F B[a]P Dibenz[ah]A Benzo[ghi]p Indino[123-cd]P
Excitation(nm)	280	270	305	305	295	305
Emission (nm)	340	360	405	430	385	430

5.0 Reagents

5.1 Mobile phases: HPLC grade acetonitrile and water, or high purity water from Milli-Q water treatment equipment.

5.2 Standard stock solutions: The standard stock solution for calibration may be purchased or prepared from ultrahigh purity grade chemicals. The standard stock solution for 16PAHs was purchased from Ultra Scientific, and 2-MNP and DBF were made from ultrahigh purity solid. This stock solution is made with high concentrations and a secondary stock solution was prepared by diluting a certain volume of the stock solution in volumetric flask. The secondary stock solution is used to make calibration standards.

5.3 Second source check standard: stock standard from another source like Supelco is purchased to check the reliability or accuracy of the calibration curves.

5.3 Mixed calibration standards: Calibration standards are prepared by combining appropriate volumes of secondary stock solutions in volumetric flasks.

6.0 Procedure

6.1 Set up the instrument with a proper method (all the operating parameters are included in operating conditions). The instrument must be allowed to become stable (stable flow, temperature, and pressure) before each analysis.

6.2 Turn on the detectors and retrieve appropriate method for fluorescence detector (emission and excitation wavelengths as defined in operating conditions)

6.3 load samples to autosampling tray

6.4 set up sample set table

6.5 press "run" button to start samples

6.6 Check if the autosampler selects the appropriate vial, and check if signals from UV and FLD are normal.

6.7 shut down flow and detectors after finishing all samples

7.0 Calculation

7.1 Minimum five-point calibration is conducted prior to analysis. Usually seven or eight concentrations are prepared. Remove concentrations that can not be detectable and concentrations that are beyond the linear range of the detector.

7.2 Determine the response factor (RSF) for each compounds: plotting chromatographic peak areas versus the concentrations, the slope of the linear curve after forcing to zero is the RSF(area/concentration) of each compound. This is applicable only if the calibration curve is linear in the range of interest and if the intercept from a calibration not forced to zero is below the quantitation limits for the analysis of interest. In general, the reciprocal of this RSF is more convenient to use and is frequently called RSF (concentration/area) in this analysis.

7.3 Determine the concentration in final solvent: the chromatographic peak areas of your samples times the RSF give the concentrations in your samples.

7.0 Quality control

Quality control checks of this SOP are based upon the DOD quality guidelines for organic analysis by high-performance liquid chromatography and slightly modified to meet specific project goals. The details of the quality control checks are summarized in Table 2.

LCS standards are also based upon DoD guidelines and are contained in the Appendix for both liquid and solid samples.

TABLE 2. SUMMARY OF QUALITY CONTROL CHECKS, DEFINITION, PURPOSE, MINIMUM FREQUENCY AND ACCEPT CRITERIA

	Definition	Purpose	Minimum frequency	Acceptance criteria
Demonstrate acceptable analyst capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analyst's ability to produce data of acceptable accuracy and precision.	Prior to using any test method and at any time there is a significant change in instrument type, personnel, or test method	QC acceptance criteria
Initial calibration for all analytes (ICAL)	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method.	To establish a calibration curve for the quantification of the analytes of interest	Minimum five-point Initial calibration for all analytes Initial calibration prior to sample analysis	linear least squares regression: $r \geq 0.995$ (r^2>0.99)
calibration verification (CV)	The verification of the initial calibration that is required during the course of analysis at periodic intervals	To verify that Instrument response is reliable, and has not changed significantly from the current initial calibration curve.	Initial calibration verification (ICV) Before sample analysis. Continue calibration verification (CCV): after every 10 field samples and at the end of the analysis sequence Response factors of the initial and end check standard added to the control chart	All analytes within ± 20% of expected value from the ICAL
Second source calibration verification (ICV)	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration.	Minimum three-point check Once after initial calibration for at least 80% of analytes	All project analytes should be within the established retention windows and the response factors of all analytes are within 20% of the expected value from ICAL.
Method detection limit (MDL) study	The process to determine the minimum concentration of a substance (analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero	At initial set-up, new method is set up or new calibrations are initiated, otherwise once per 12 month period; otherwise quarterly MDL verification checks shall be performed	MDL verification checks must produce a signal at least 3 times the instrument's noise level.
Method blank	A sample of a matrix similar to the batch of associated samples (when available) in which no target analytes or interferences are present at concentrations that impact the analytical results. It is processed simultaneously with samples of similar matrix and under the same conditions as the samples.	To assess background interference or contamination in the analytical system that might lead to high bias or false positive data. Results of method blanks provide an estimate of the within-batch variability of the blank response and an indication of bias introduced by the preparation and analytical procedure	One per preparatory batch	No analytes detected > ½ RL (reporting limit). For common laboratory contaminants, no analytes detected at > RL, or does not interference with sample concentration
Reagents blank	The solvent used for preparing samples	To check the possible interference from the solvent, and clean the system for possible carryover	Before initial run, every 10 samples or one group of samples, and	No analytes detected > ½ RL (reporting limit). Or does not interference with sample concentration
Laboratory control sample (LCS) containing all analytes required to be reported (LCS samples are not applicable to this study; see Section 3.2.2)	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is analyzed using the same sample preparation, reagents, and analytical methods employed for regular samples.	To evaluate method performance by assessing the ability of the laboratory/analyst to successfully recover the target analytes from a control (clean) matrix. Control limits for LCS recovery, typically expressed as percent recovery, are used for the development of statistical control limits and serve as acceptance criteria for determining whether an analytical run is in control	Triplicates before new method and new matrix, then repeated as necessary (not applicable to water samples for direct injection and SPME fiber samples that do not involve sample transition)	DoD generated LCS-CLs will be used if available (see appendix)
Duplicate sample (replicate)	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are prepared and analyzed identically	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intra-laboratory analytical process for a specific sample matrix	A minimum three replicates for identification of mean, and at least four replicates for statistical analysis	RPD ≤ 20%

If any of the acceptance criteria are not satisfied, correct the problem and redo the quality control check.

APPENDIX

TABLE A1 LCS CONTROL LIMITS FOR POLYNUCLEAR AROMATIC HYDROCARBONS SW-846 METHOD 8310 WATER MATRIX

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Acenaphthene	70	11	35	105	25	115
Acenaphthylene	74	13	35	115	20	125
Anthracene	77	12	40	110	30	125
Benz[a]anthracene	81	11	50	110	40	125
Benzo[a]pyrene	79	11	45	115	35	125
Benzo[b]fluoranthene	82	10	50	110	40	125
Benzo[k]fluoranthene	79	10	50	110	40	120
Benzo[g,h,i]perylene	77	14	35	120	20	135
Chrysene	83	11	50	115	40	125
Dibenz[a,h]anthracene	64	15	20	110	10	125
Fluoranthene	82	11	50	115	35	125
Fluorene	69	11	35	105	25	115
Indeno[1,2,3-cd]pyrene	80	11	45	110	35	125
Naphthalene	68	12	35	105	20	115
Phenanthrene	80	13	40	120	25	135
Pyrene	80	9	50	110	45	115

TABLE A2 LCS CONTROL LIMITS FOR POLYNUCLEAR AROMATIC HYDROCARBONS SW-846 METHOD 8310 SOLID MATRIX

Analyte	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit	Lower ME Limit	Upper ME Limit
Acenaphthene	71	12	35	110	20	120
Acenaphthylene	73	13	35	115	20	125
Anthracene	86	13	45	125	35	140
Benz[a]anthracene	78	9	50	105	40	115
Benzo[a]pyrene	86	15	40	135	25	150
Benzo[b]fluoranthene	89	11	55	120	45	130
Benzo[k]fluoranthene	84	12	50	120	35	135
Benzo[g,h,i]perylene[20]	85	10	55	115	45	125
Chrysene	87	11	55	120	45	130
Dibenz[a,h]anthracene	81	11	45	115	35	125
Fluoranthene	88	16	40	135	25	150
Fluorene	76	10	45	105	35	115
Indeno[1,2,3-cd]pyrene	95	13	55	135	45	145
Naphthalene	80	11	50	110	40	120
Phenanthrene	91	12	55	125	45	135
Pyrene	82	11	50	115	40	125

ReferenceU.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste physical/chemical methods, 3rd ed. Method 8310. SW-846. Office of Solid Waste and Emergency Response, Washington, DC.

STANDARD OPERATING PROCEDURE: Liquid-liquid extraction for aqueous organics via separatory funnel

Title: Liquid-liquid extraction for aqueous organics via separatory funnel

11.0 Purpose/Applicability

This SOP is based upon EPA method 3510 in SW-846 series and describes a procedure for isolating organics from aqueous samples. This SOP was modified and developed specifically for the laboratory SPME calibration study contracted from USACE. The organics in this study include polycyclic aromatic hydrocarbons (PAHs) and Dibenzofuran (DBF)

12.0 Summary of Method

A measured volume of sample, here is 150 ml, is serially extracted with Methylene chloride using a separatory funnel. The extract is dried, concentrated, exchanged into acetonitrile for HPLC analysis

13.0 Interferences

Unwanted organic chemicals can be introduced into the sample extract through contaminated reagents, glassware, chemicals or through poor technique. Reagent and sample blanks are analyzed to insure that contaminants are not introduced into the sample extract.

14.0 Apparatus

14.1 250-ml seperatory funnel with Teflon stopcock

14.2 10 mm I.D. glass buret or Glass funnel as drying column

14.3 Nitrogen blow down system for concentrating extract

15.0 Reagents

HPLC grade Methylene chloride and Acetonitrile

16.0 procedure

16.1 ADD an accurately measured volume of sample to the separatory funnel.

16.2 Add 10ml of Methylene chloride to the separatory funnel, seal and shake the funnel vigorously for 1-2 minutes with periodic venting to release excess pressure

16.3 Allow the organic (bottom) layer to separate from the aqueous layer for a minimum of ten minutes. If an emulsion forms, attempt to disrupt it with stirring, centrifugation or filtration. Drain the organic layer into a 40ml brown sample vial to retain the aqueous phase in the seperatory funnel.

16.4 Repeat the extraction two additional times using fresh portions of solvent. Combine the three solvent extracts.

16.5 Dry the extract by passing it through a drying column or funnel containing sodium sulfate. Collect the dried extract in a sampling tube for nitrogen blow down.

16.6 Concentrate the extract to 2 ml and then solvent exchange into acetonitrile for HPLC analysis

17.0 Quality control

17.1 All quality control data should be maintained and available for easy reference or inspection

17.2 At least two sample blanks are analyzed to check the background PAH concentrations

17.3 Laboratory control samples are prepared by spiking site water at concentrations high enough to be detectable by direct injection on HPLC. Two LCS are analyzed before, in the middle and after the whole calibration study. The extraction efficiencies of each compound are calculated by comparing the concentration by liquid-liquid extraction and the concentration by direct injection by HPLC. This extraction efficiency is used to correct the measured aqueous concentrations of PAHs and DBF.

Reference

U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid waste physical/chemical methods, 3rd ed. Method 3510C. SW-846. Office of Solid Waste and Emergency Response, Washington, DC.

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APPENDIX D

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QUALITY ASSURANCE SURVEILLANCE PLAN

For **Solid-phase Microextraction Deployment at PSR**
Contract Number: W912DW-09-P-0283
Contract Description: Purchase Order
Contractor's name: Danny Reible, University of Texas
(hereafter referred to as the contractor).

Revision 2: 17 September 2010

1. PURPOSE.

This Quality Assurance Surveillance Plan (QASP) provides a systematic method to evaluate performance for the stated contract. This QASP explains the following:

- What will be monitored.
- How monitoring will take place.
- Who will conduct the monitoring.
- How monitoring efforts and results will be documented.

This QASP does not detail how the contractor accomplishes the work. Rather, the QASP is created with the premise that the contractor is responsible for management and quality control actions to meet the terms of the contract. It is the Government's responsibility to be objective, fair, and consistent in evaluating performance. In addition, the QASP should recognize that unforeseen and uncontrollable situations may occur.

This QASP is a "living document" and the Government may review and revise it on a regular basis. However, the Government shall coordinate changes with the contractor. Updates shall ensure that the QASP remains a valid, useful, and enforceable document. Copies of the original QASP and revisions shall be provided to the contractor and Government officials implementing surveillance activities.

The following FAR clauses may apply:

52.246-4 Inspection of Services – Fixed-Price,

2. GOVERNMENT ROLES AND RESPONSIBILITIES.

The following personnel shall oversee and coordinate surveillance activities.

a. Contracting Officer (KO) - The KO shall ensure performance of all necessary actions for effective contracting, ensure compliance with the contract terms, and shall safeguard the interests of the United States in the contractual relationship. The KO shall also assure that the contractor receives impartial, fair, and equitable treatment under this contract. The KO is ultimately responsible for the final determination of the adequacy of the contractor's performance.

Assigned KO: Susan Newby
Organization or Agency: Seattle District, US Army Corps of Engineers, Seattle
Telephone: 206.764.6754
Email: Susan.F.Newby@usace.army.mil

b. Acquisition Manager (AM) - The AM acts as an acquisition consultant and serves as liaison between the TRICARE Procurement Support Office (TPS) and the requesting program office, as well as liaison between the TRICARE Management Activity (TMA) and the supporting contracting office.

Assigned AM: George Barnes
Telephone: 206.764.6801
Email: George.E.Barnes@usace.army.mil

c. Contracting Officer's Representative (COR) - The COR is responsible for technical administration of the contract and shall assure proper Government surveillance of the contractor's performance. The COR shall keep a quality assurance file. At the conclusion of the contract or when requested by the KO, the COR shall provide documentation to the KO. The COR is not empowered to make any contractual commitments or to authorize any contractual changes on the Government's behalf. The contractor shall refer any changes they deem may affect contract price, terms, or conditions to the KO for action.

Assigned COR: Travis C. Shaw
Telephone: Seattle District, US Army Corps of Engineers, Seattle
Email: Travis.C.Shaw@usace.army.mil

d. Other Key Government Personnel -

Title: Ms Mandy Michalsen, Technical Lead
Telephone: 206.764.3324
Email: Mandy.M.Michalsen @usace.army.mil

3. CONTRACTOR REPRESENTATIVES:

The following employees of the contractor serve as the contractor's Program Manager and Task Manager for this contract.

a. Principal Investigator -
Telephone:
Email:

b. Other Contractor Personnel -
Title:
Telephone:
Email:

4. PERFORMANCE STANDARDS.

These consist of meeting performance standards listed in Table 4. Completeness (i.e., compliance) with 90% of the compound-wise values is the performance standard.

5. INCENTIVES.

The Government will use no incentives for this work.

6. METHODS OF QA SURVEILLANCE.

The COR will use the surveillance method listed below in the administration of this QASP.

Analysis of contractor's progress reports. This method involves comparison to achieved limits of performance (see Section 4, Performance Standards, above).

Surveillance results may be used as the basis for actions (to include payment deductions) against the contractor. In such cases, the Inspection of Services clause in the Contract becomes the basis for the KO's actions.

8. RATINGS.

Metrics and methods are designed to determine if performance exceeds, meets, or does not meet a given standard and acceptable quality level. A rating scale shall be used to determine a positive, neutral, or negative outcome. The following ratings shall be used:

EXCEPTIONAL:	Performance meets contract requirements to the Government's benefit.
SATISFACTORY:	Performance meets some but not all contractual requirements but provides partially or mostly usable information.
UNSATISFACTORY:	Performance does not meet contractual requirements with the result that the calibration test is invalid.

9. DOCUMENTING PERFORMANCE.

a. ACCEPTABLE PERFORMANCE.

The Government shall document positive performance. A report template is attached. Any report may become a part of the supporting documentation for fixed fee payments, award fee payments, or other actions.

b. UNACCEPTABLE PERFORMANCE.

When unacceptable performance occurs, the COR shall inform the contractor. This will normally be in writing unless circumstances necessitate verbal communication. In any case the COR shall document the discussion and place it in the COR file.

When the COR determines formal written communication is required, the COR shall prepare a Contract Discrepancy Report (CDR), and present it to the contractor's task manager or on-site representative. A CDR template is attached to this QASP.

The contractor shall acknowledge receipt of the CDR in writing. The CDR will specify if the contractor is required to prepare a corrective action plan to document how the contractor shall correct the unacceptable performance and avoid a recurrence. The CDR will also state how long after receipt the contractor has to present this corrective action plan to the COR. The Government shall review the contractor's corrective action plan to determine acceptability.

10. FREQUENCY OF MEASUREMENT.

a. Frequency of Measurement.

During contract/order performance, the COR shall be in close communication with the laboratory, and shall review the work product.

b. Frequency of Performance Assessment Meetings.

The COR shall teleconference with the contractor once during the period of performance to assess performance and shall provide a written assessment.

Prepared by: John S. Wakeman

_____
Signature – Contracting Officer's Representative
Travis C. Shaw

PERFORMANCE REPORT

1. CONTRACT NUMBER: W912DW-09-P-0283

2. Prepared by**:** (Name of COR) Travis C. Shaw

3. Date and time of observation**:**

4. **Observation:**

<Examples of items to include in a report are:
- Method of surveillance.
- How frequently you conducted surveillance.
- Surveillance results.
- Number of observations.>

Prepared by: Travis C. Shaw

_____ _____
Signature – Contracting Officer's Representative Date

CONTRACT DISCREPANCY REPORT (CDR)

1. Contract Number: W912DW-09-P-0283

2. TO: (Contractor Task Manager or on-site representative):

3. FROM: (Name of COR) Travis C. Shaw

4. Date and time observed **discrepancy:**

5. **DISCREPANCY OR PROBLEM:**

<Describe in detail. Identify any attachments.>

5. Corrective action plan:

A written corrective action plan < is / is not > required.

< If a written corrective action plan is required include the following. > The written Corrective Action Plan will be provided to the undersigned not later than < # days after receipt of this CDR. >

Prepared by: Travis C. Shaw

_____ _____
Signature – Contracting Officer's Representative Date

Received by:

_____ _____
Signature - Contractor Task Manager or on-site representative Date